

# THE AMERICAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL SOCIETY OF AMERICA

Vol. 25

FEBRUARY, 1940

No. 2

## EFFECT OF DYES ON THE CRYSTAL HABIT AND OPTICS OF NaF, LiF, NaCl, KCl, KBr AND KI

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### ABSTRACT

The effect of 112 dyes on the crystal habit and optics of NaF, LiF, NaCl, KCl, KBr and KI was investigated experimentally. A few dyes are adsorbed on {111} and cause variation from the ordinary cubical habit to octahedral. Most dyes are adsorbed, if at all, by {100}. Habit variation is favored by a slow rate of growth of the crystals.

The nature of the adsorption mechanism is obscure. Adsorption control by the substitutional attachment of polar groups in the dye molecule into the structure of the adsorbing crystal, of the nature found by Buckley for the adsorption of dyes by oxyalts, appears from structural considerations to be very improbable. Dye adsorption mechanisms of the types described by Kolthoff and by Verwey for AgCl also appear to be inadequate to account for the observed effects. France's theory of adsorption by charged planes is found to be largely at variance with observation, and the theory itself is shown to be subject to a

\* The experimental work described herein was done at the Massachusetts Institute of Technology, Cambridge, Mass.

restriction which denies any application to the growth and adsorption phenomena of macroscopic crystals.

Many instances of anomalous pleochroism were observed. No connection was found between the occurrence of pleochroism and habit variation, nor could either of these effects be identified with special characters of the dyes concerned. Dyes have a marked skeletonizing effect on crystals of NaF and LiF. The effect is lacking with the alkali chlorides, bromides and iodides. Strong adsorption of dye, as evidenced by habit variation or a special skeletonizing effect, is accompanied by a tendency for supersaturation in the crystallizing solution.

## INTRODUCTION

Crystals may change their habit and become colored and sometimes pleochroic when grown from solutions to which a dye has been added. Particular mention may be made of the pioneer work in this field by de Senarmont, in 1854, and of the recent studies by Gaubert, France and co-workers, and Buckley. A list of substances on which the effect of dyes has been investigated is given in Table 1. Extended reviews of the work with dyes, in correlation with other crystal-adsorption and crystal-orientation phenomena relevant to the subject of anomalous mixed crystals, have been given by Spangenberg and Neuhaus (1) and by Seifert (2).

The present paper deals with the effect of dyes on the habit and optics of NaF and other alkali halides of the NaCl structural-type. The influence of inorganic cosolutes and of organic cosolutes aside from dyes on NaF and other halides is described in an accompanying paper.

## DESCRIPTION OF EXPERIMENTAL METHODS

Two different methods of crystallization were employed. With NaF, NaCl and LiF, 100 to 300 cc. of the dye-containing solution were evaporated at 80° to about half the original volume. The evaporation was usually so arranged as to take from 20 to 36 hours. Glass wool was added to the solutions to permit crystals to develop freely suspended in the solution.

Crystallization from large volume was found unsuited to KCl, KBr and KI, because of "creeping" and temperature-solubility effects noted below, and recourse was made to crystallization on microscope slides. The following technique was used. The dye was dissolved in a drop of water contained in a small beaker and 10 cc. of hot saturated alkali halide solution added thereto. A large deep drop of this solution was then formed on a hot microscope slide, and crystallization followed under the microscope. Crystals appear and grow with great rapidity, due to the marked change in solubility with temperature. The drop when cooled to room temperature consists of a slushy mass of crystals. This slush was then raked to one side, and a clear portion of the drop allowed to crystal-

TABLE 1. INDEX TO LITERATURE OF DYE-CRYSTAL SYSTEMS

Crystallized substance	Reference	Crystallized substance	Reference
AgBr	54	NH <sub>4</sub> ClO <sub>4</sub>	54
AgCl	54, 57	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	26
Ba(NO <sub>3</sub> ) <sub>2</sub>	13, 14, 17, 22, 23, 36, 55, 68	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	68
BaSO <sub>4</sub>	53	NH <sub>4</sub> H malate	25, 76
BaCl <sub>2</sub> · 2H <sub>2</sub> O	68	NH <sub>4</sub> NO <sub>3</sub>	68
CaCO <sub>3</sub>	56, 66	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	68
CaC <sub>2</sub> O <sub>4</sub> · H <sub>2</sub> O	68	NH <sub>4</sub> tartrate	25, 76
CaSO <sub>4</sub> · 2H <sub>2</sub> O	12, 24, 46	Pb(NO <sub>3</sub> ) <sub>2</sub>	13, 17, 22, 23, 27, 31, 36, 39, 43, 48, 49, 55, 68
Cs alum	20	RbH malate	25
CuSO <sub>4</sub> · 5H <sub>2</sub> O	28, 33	Sr(NO <sub>3</sub> ) <sub>2</sub>	13, 14, 23, 55, 68
H <sub>3</sub> AsO <sub>4</sub> · $\frac{1}{2}$ H <sub>2</sub> O	67	Sr(NO <sub>3</sub> ) <sub>2</sub> · 4H <sub>2</sub> O	2, 3, 15, 28, 30, 32, 68
K alum	16, 19, 20, 21, 31, 34, 36, 38, 68	TIH malate	26
KBr	68	TI <sub>2</sub> SO <sub>4</sub>	28
KBrO <sub>3</sub>	68	ZnCl <sub>2</sub> · H <sub>2</sub> O	28
KCl	4, 55, 68	ZnSO <sub>4</sub> · 7H <sub>2</sub> O	16, 68
KClO <sub>4</sub>	54, 70, 73	Acetanilid	60
KClO <sub>3</sub>	16, 54, 68, 69, 74	Alkaloid tartrates	76
KH <sub>2</sub> PO <sub>4</sub>	68	Asparagine	76
KI	68	Anilic acid	50
KIO <sub>3</sub>	68	Benzoin	50, 60
KNa tartrate	2, 16	Benzamid	60
KNO <sub>3</sub>	2, 68	Benzophenone	60, 62
K <sub>2</sub> SO <sub>4</sub>	52, 55, 58, 59, 68, 69, 70, 71, 72, 81	Bromnitrobenzene	60
MgCl <sub>2</sub> · 6H <sub>2</sub> O	68	Chlornitrobenzene	62
MgNH <sub>4</sub> sulphate	68	Cinchonamine	62
MgSO <sub>4</sub> · 10H <sub>2</sub> O	68	Cinchone tartrate	76
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> · 10H <sub>2</sub> O	2, 68	Cinnamic acid	61
NaBr	68	Codeine	62
NaBr · 2H <sub>2</sub> O	68	Dibromobenzene	62
NaCl	1, 55, 64, 68	Dinitrobenzene	60
NaClO <sub>3</sub>	8, 16, 68, 75	Erythritol	51
NaF	64	Formanilid	60
Na <sub>2</sub> HPO <sub>4</sub> · 12H <sub>2</sub> O	68	Haematoxylin	50
NaI · 2H <sub>2</sub> O	68	Helenine	80
NaNO <sub>2</sub>	2, 18, 68	Hippuric acid	50
Na <sub>2</sub> SO <sub>4</sub>	68	Liquid crystals, etc.	25, 40, 41, 77
Na <sub>2</sub> SO <sub>4</sub> · 10H <sub>2</sub> O	68	Maleic acid	50
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> · 5H <sub>2</sub> O	68	Meconic acid	37, 47, 50
Na tartrate	25, 76	Mesaconic acid	50
NH <sub>4</sub> Br	1, 68	Metaoxybenzoic acid	61
NH <sub>4</sub> Cl	1, 68	Morphine	28
		Naphthalene	82



TABLE 1. INDEX TO LITERATURE OF DYE-CRYSTAL SYSTEMS—*Continued*

Crystallized substance	Reference	Crystallized substance	Reference
Narceine	9, 50	Succinamid	50
Oxalic acid	16, 42, 61	Succinic acid	50, 61
Papaverine	50	Sugar	2, 9
Paraoxybenzoic acid	61	Sulphonal	62
Phlorizin	6, 7, 47	Terpinol	62
Phthalic acid	11, 29, 45, 47, 50, 61, 68	Tetrachlorobenzene	62
Phloroglucinol	78	Thiourea	50
Picric acid	49	Thymol	10
Piperonal	62	Trional	62
Protocatechuic acid	50, 61	Urea nitrate	5, 12, 44, 47, 49
Quinine sulphate	50	Urea oxalate	5, 47, 49
Salol	60	Uric acid	79
Strychnine tartrate	76	Vanillin	51, 62, 80
		Veratric acid	50

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lize slowly by evaporation at room temperature. It is important to investigate both conditions of slow and of fast growth, since the habit-modifying effect of a cosolute may vary therewith.

The dye concentration was arbitrarily fixed at 0.03 g./100 cc. solution for NaF and NaCl, at 0.01 g./100 cc. for LiF, and at 0.01 g./10 cc. for KCl, KBr and KI. These amounts were frequently above the solubility of the dye. In many instances supplementary crystallizations were made at other dye concentrations; these are indicated in Table 2, summarizing the experimental data. No effort was made to estimate the minimum dye concentration necessary to effect habit variation, as was done in the work of Buckley.

Crystallizations made on a microscope slide are not very satisfactory, and this method was adopted only in lack of a practical alternative. There is a special tendency for the development of skeletonized or composite forms, some of which may simulate modified crystals. The instances of habit variation found in KCl, KBr and KI by this procedure, and described on following pages, were accepted only after repeated verification. It may also be noted that the small size of the crystals obtained on microscope slides usually precludes recognition of their color or pleochroism.

#### TABULATION OF EXPERIMENTAL RESULTS

The observed effect of dyes on the crystal habit of NaF, LiF, NaCl, KCl, KBr and KI is summarized in Table 2. The presence of the dye in the crystallizing solutions was also found in many instances to be accompanied by the development of pigmentation and anomalous pleochroism in the crystals, by super-saturation and rate-of-growth phenomena, and by the development of skeletal growths. These effects are described in following sections.



TABLE 2. TABULATION OF EXPERIMENTAL RESULTS WITH DYES

Dye concentration = 0.03 g./100 cc. solution for NaF and NaCl, 0.01 g./100 cc. for LiF, and 0.01 g./10cc. for KCl, KBr and KI. Supplementary crystallizations at other dye concentrations are indicated in footnotes. The pure-solution habit of the halides listed is cubic.

Colour index number refers to the Colour Index: *Society of Dyers and Colourists*, Bradford, Yorkshire, 1924, E. M. Rowe, editor.

Key to symbols:  $a = \{100\}$ ;  $o = \{111\}$ .

Colour index	Dye	Acid NaF <sup>4</sup>	LiF	NaCl	KCl	KBr	KI	Acid NaF <sup>4</sup>
5	Napthol Green B	$a^1$	$a$	$a$	$a$	$a$		$a$
9	Martius Yellow	$a$						$a$
10	Napthol Yellow S	$a^1$	$a$	$a$	$a^3$			$a$
16	Fast Yellow G	$a$	$a$	$a$		$a$	$a$	$a$
21	Chrysoidine R	$a$		$a$	$a$	$a$	$a$	$a$
26	Croceine Orange	$o^1$	$a$	$a^1$	$a^3$	$a^3$	$a^3$	$a$
27	Orange G	$a$	$a$	$a$				$a$
29	Chromotrope 2R	$a$			$a^3$	$a$	$a$	$a$
30	Acid Fuchsine	$a$				$a^3$	$o$	$a$
31	Pontacyl Carmine 2G	$a$	$a$	$a$	$a$	$a$	$a$	$a$
40	Pontachrome Yellow 3RN	$a$		$a$	$a$			
56	Chromotrope 6B	$a$				$a$	$a$	$a$
57	Pontacyl Carmine 6B	$a$	$a$			$a$		$a$
63	Orange GT	$a$						$a$
77	Palatine Scarlet	$a^2$	$a$	$a$	$a$			$a$
79	Xylidine Red	$a^2$	$a$	$a$				$a$
80	Ponceau 3R	$a$	$a$					
88	Bordeaux B	$a$						$a$
89	Crystal Ponceau	$a$	$a$	$a$				$a$
98	Chrome Brown R	$a$						
99	Chrome F	$a$						$a$
138	Metanil Yellow	$a$	$a$	$a$	$a$			$a$
142	Orange III	$a$	$a$	$a$	$a$			
143	Orange IV	$a$	$a$	$a$				
144	Brilliant Yellow S	$a$	$a$	$a$	$a^3$	$a$	$o$	
148	Resorcin Yellow	$a$	$a$	$a$	$a$			$a$
150	Orange I	$a$	$a$	$a$	$a$			
151	Orange II	$a$						
161	Orange RO	$a$						
170	Solochrome Black	$o^2$		$a^1$		$a$		$a$
176	Fast Red A	$a^1$		$a$	$a$			$a$
179	Azorubin	$a$	$a$	$a$	$a$			
180	Fast Red VR	$a$		$a$	$a$			
181	Azo Red A	$a$						
182	Aceko Fast Red	$a$						
183	Newport Croceine Scarlet	$a$						
184	Amaranth	$a$						

TABLE 2. TABULATION OF EXPERIMENTAL RESULTS WITH DYES—*Continued*

Colour index	Dye	Acid NaF <sup>4</sup>	LiF	NaCl	KCl	KBr	KI	Acid NaF <sup>4</sup>
185	Brilliant Scarlet	<i>a</i> <sup>2</sup>		<i>a</i>	<i>a</i>			
186	Ponceau 6R	<i>a</i>	<i>a</i>	<i>a</i>				
188	Chromotrope 8B	<i>a</i>						
197	Superchrome Yellow RN	<i>a</i>		<i>a</i> <sup>3</sup>	<i>o</i> <sup>3</sup>	<i>a</i> <sup>3</sup>	<i>a</i> <sup>3</sup>	
203	Pontachrome Black K	<i>a</i>						
204	Solochrome Black A	<i>a</i>						
252	Croceine Scarlet N ex.	<i>a</i>						
277	Croceine Scarlet 3B	<i>a</i> <sup>1</sup>	<i>a</i>	<i>a</i>	<i>a</i>			
280	Biebrich Scarlet	<i>a</i>						
286	Croceine Scarlet 7B	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>			
310	Naphthyl Blue-Black N	<i>a</i>		<i>a</i>	<i>a</i>			
311	Naphthol Black 6B	<i>a</i>		<i>a</i>	<i>o</i>			<i>a</i>
313	Brilliant Croceine 9B	<i>a</i> <sup>2</sup>	<i>a</i>	<i>a</i> <sup>2</sup>	<i>o</i> <sup>3</sup>	<i>o</i> <sup>3</sup>	<i>a</i>	<i>a</i>
314	Diamine Blue 6G	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>			
315	Naphthol Black 3B	<i>a</i> <sup>1</sup>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>		
316	Diaminogen Blue NA	<i>a</i>		<i>a</i>	<i>a</i>			
353	Pontamine Fast Pink BL	<i>a</i> <sup>2</sup>	<i>a</i>	<i>a</i> <sup>1</sup>	<i>a</i>			
370	Congo Red	<i>a</i>	<i>a</i>					
406	Pontamine Blue BBF	<i>a</i>		<i>a</i>	<i>o</i> <sup>3</sup>			
443	Acid Anthracene	<i>a</i>	<i>a</i>					<i>a</i>
448	Benzopurpurin 4B	<i>a</i>	<i>a</i>					
449	Benzopurpurin 6B	<i>a</i>						
463	Azo Blue	<i>a</i> <sup>2</sup>	<i>a</i>	<i>a</i>				
471	Dianil Azarine	<i>a</i> <sup>1</sup>		<i>a</i> <sup>1</sup>				
472	Diamine Blue BX	<i>a</i> <sup>2</sup>	<i>a</i>	<i>a</i> <sup>1</sup>	<i>a</i>			
473	Columbia Blue G	<i>a</i> <sup>1</sup>		<i>a</i>	<i>a</i>	<i>a</i>		
474	Chicago Blue R	<i>a</i>		<i>a</i>	<i>a</i>			
477	Newport Direct Blue 3B	<i>a</i> <sup>2</sup>	<i>a</i>	<i>a</i>	<i>a</i>			
480	Chrysamine R	<i>a</i>						
475	Eboli Blue 6A	<i>a</i>		<i>a</i>	<i>a</i>			<i>a</i>
512	Chicago Blue RW	<i>a</i>		<i>a</i>	<i>a</i>		<i>a</i>	<i>a</i>
520	Diamine Sky Blue A	<i>a</i> <sup>1</sup>						
582	Direct Deep Black E ex.	<i>a</i>		<i>a</i>	<i>a</i>			
621	Direct Orange G	<i>a</i>			<i>a</i>			
622	Pontamine Yellow XSG	<i>a</i>		<i>a</i>	<i>o</i> <sup>3</sup>			
624	Diphenyl Citronine G	<i>a</i>			<i>a</i>			
640	Tartrazine	<i>a</i>	<i>a</i>	<i>a</i>				
655	Auramine	—	<i>a</i>					
657	Malachite Green	—						
670	Light Green SF yellowish	<i>a</i> <sup>1</sup>						
677	Basic Fuchsin	<i>a</i>						
680	Methyl Violet	<i>a</i>			<i>a</i>			
680	Gentian Violet	<i>a</i>						
681	Crystal Violet	<i>a</i> <sup>1</sup>						
692	Acid Magenta	—						

TABLE 2. TABULATION OF EXPERIMENTAL RESULTS WITH DYES—*Continued*

Colour index	Dye	Acid NaF <sup>4</sup>	LiF	NaCl	KCl	KBr	KI	Acid NaF <sup>4</sup>
695	Acid Violet 4BN	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>			
698	Formyl Violet S4B	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	
703	Methyl Alkali Blue	<i>a</i> <sup>1</sup>						
707	Soluble Blue	<i>a</i>						
712	Patent Blue	<i>a</i> <sup>1</sup>				<i>a</i>	<i>a</i>	
715	Cyanol Extra	<i>a</i> <sup>1</sup>	<i>a</i>	<i>a</i> <sup>1</sup>	<i>a</i> <sup>3</sup>	<i>a</i>	<i>a</i>	
749	Rhodamine B	<i>a</i>		<i>a</i>	<i>a</i>			
766	Uranine	<i>a</i>						
766	Fluoresceine	<i>a</i>		<i>a</i> <sup>2</sup>	<i>a</i>			
768	Eosine	<i>a</i> <sup>1</sup>						
773	Erythrosine	<i>a</i> <sup>1</sup>		<i>a</i>	<i>a</i>			
774	Phloxine	<i>a</i>		<i>a</i>	<i>a</i>			
777	Rose Bengale	<i>a</i>		<i>a</i>	<i>a</i>			
779	Rose Bengale 3B	<i>a</i>		<i>a</i>	<i>a</i>			
801	Quinoline Yellow	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>			
841	Safranine A	<i>a</i> <sup>1</sup>		<i>a</i>	<i>a</i>			
842	Methylene Violet 2RA	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	
861	Induline Soluble	<i>a</i>						<i>a</i>
865	Nigrosine WSB	<i>a</i>						
922	Methylene Blue	<i>a</i> <sup>1</sup>						
1027	Alizarin NAC 20%	<i>a</i>						
1081	Anthraquinone Green GX	<i>a</i> <sup>2</sup>	<i>a</i>	<i>a</i>	<i>a</i>			
1034	Alizarin Red S	<i>a</i> <sup>2</sup>		<i>a</i> <sup>1</sup>	<i>a</i> <sup>3</sup>	<i>a</i>	<i>a</i>	<i>a, o</i>
1085	Alizarin Blue Black B	<i>a</i> <sup>1</sup>		<i>a</i>	<i>a</i> <sup>3</sup>			
1087	Alizarin Cyanol EF	<i>a</i>						
1089	Anthraquinone Blue SR	<i>a</i> <sup>2</sup>		<i>a</i> <sup>1</sup>				
1180	Acid Blue GR conc.	<i>a</i>						
1238	Turmeric	<i>a</i> <sup>1</sup>						
1239	Cochineal	<i>a</i>						
1246	Haematoxylin	<i>a</i> <sup>2</sup>						

<sup>1</sup> Also at 0.1 and 0.01 g. dye/100 cc. solution.<sup>2</sup> Also at 0.1, 0.01 and 0.001 g. dye/100 cc. solution.<sup>3</sup> Also at 0.05 and 0.001 g. dye/100 cc. solution.<sup>4</sup> Solution containing 1 cc. 6N HCl per 100 cc.



## DESCRIPTION OF HABIT VARIATION AND OPTICAL EFFECTS

## EFFECT OF DYES ON NaF

*Habit Variation.* Four of the 112 dyes tried with NaF effected variation in habit from cubic to octahedral. The effective dyes were Croceine Orange, Solochrome Black, Alizarin Red S, and Haematoxylin. Only a crude Haematoxylin preparation was available, and parallel results were not obtained in check crystallizations. The octahedra obtained with this substance and with Alizarin Red S were deep red to red-brown in color.

The presence of free alkali has been found (3) to increase the habit-varying property of dyes containing carboxyl groups and to decrease the effectiveness of sulphonate dyes containing hydroxyl groups. No experi-

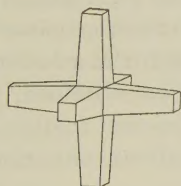


FIG. 1

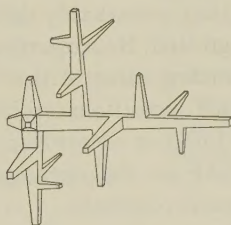


FIG. 2

ments in this direction were made with NaF since free hydroxyl itself is markedly effective in changing the habit of NaF. The addition of free acid (HCl) to the solutions was found to be without action on many of the non-effective dyes (Table 2), although it markedly favored the formation of normal cubes in place of the skeletal cubes, described beyond, commonly obtained with NaF from solutions containing dyes. The effective dyes, Croceine Orange and Solochrome Black, however, lost their effectiveness in acid solutions. Alizarin Red S remained effective in faintly acid solutions.

*Skeletal Growths.* Skeletonized cubes of NaF were obtained quite generally from solutions containing the ineffective dyes. A few dyes, notably Anthraquinone Green GX, were without a marked skeletonizing effect. This is a special effect associated with the presence of dye, since NaF crystallizes from pure water solutions as ordinary cubes. Moreover, the effect is found only with NaF and LiF and is almost always lacking with the alkali chlorides, bromides and iodides. The skeletal growths typically consist of six tapering arms at  $90^\circ$  to each other and bounded laterally and at the terminations by  $\{100\}$  faces (Figs. 1 and 2). The degree of complexity of the growths varies from cubical forms with short stubby arms extending from one or more faces to complex, rectangular, lattice-like growths with hundreds of subsidiary branching arms. The growths

usually range in size from 1 to 3 mm., but occasionally extend up to 10 mm. or more. Most crystallizations afford the simple type of Fig. 1 mixed with a small proportion of ordinary cubes and more complex growths.

The action of different dyes in promoting skeletal growths varies widely. In particular, Fast Red A, Diaminogen Blue NA, Pontamine Fast Pink BL, Direct Deep Black E, Pontamine Yellow XS and Cochineal caused the development of extraordinarily complex and delicate lattice-like growths, together with needle-like single-crystal cubes a centimeter or more in length. These growths formed in the solution as dense bulbous aggregates of a pasty consistency. Similar effects can be obtained with other dyes at relatively high concentrations. Buckley has also noted (4) that remarkably delicate skeletal growths are produced in  $\text{KClO}_3$  by Congo Red, Benzopurpurin 4B and other colloidal dyes.

The skeletonizing effect of the dyes is lost if the solutions are made acid. Under such conditions ordinary cubes are obtained, which, however, may be tinted or pleochroic as from non-acid solutions. Skeletonized cubes of NaF are also obtained from solutions containing hydroxyl-affording inorganic cosolutes.

*Crystallization-Interference Effects.* Many dyes were found to cause super-saturation in solutions of NaF and the other alkali halides. In general, the effect was most marked in NaF with dyes that possessed a special skeletonizing influence, or that caused habit variation. It was also remarked that dyes which effected habit variation in one halide and not in others had a relatively marked influence on the super-saturation of the unmodified halides.

Similar observations have been made by Wenk (5) and by Marc and Wenk (6), who found that marked super-saturation was induced in  $\text{K}_2\text{SO}_4$  and other substances by dyes which strongly colored the crystals or which modified their habit. Yamamoto (7) found that the particular cosolutes which increased the size of KCl and  $\text{NH}_4\text{Cl}$  crystals produced super-saturation in solutions of those substances.

The super-saturation in these instances is a result of the adsorption of the dye or cosolute on the nuclei tending to form in the solution, peptizing them and, in a sense, forcing them back into solution. When nuclei are finally forced through the threshold size barrier by increasing super-saturation, the adsorption may be expressed by a pigmentation of the crystals, by habit variation, or by an increase in the average size of the crystals as a consequence of the fewer number of nuclei present in the solution. The adsorption may also, by slowing the over-all rate of growth of the crystals, increase their perfection and transparency.

*Coloration.* Many dyes were found to afford deeply colored cubes or skeletal cubes of NaF. These dyes are listed in Table 3. A number of instances of faint coloration were excluded from this list. The occurrences are significant in that they identify {100} as the selectively adsorbing plane. No habit variation accompanies such adsorption since {100} is the ordinary habit of NaF.

TABLE 3. DYES ADSORBED BY {100} OF NaF

Croceine Orange	Diaminogen Blue NA	Pontamine Yellow XSG
Pontachrome Yellow 3RN	Pontachrome Fast Pink BL	Diphenyl Citronine G
Chromotrope 6B	Pontachrome Blue BBF	Acid Violet 4BN
Bordeaux B	Acid Anthracene	Formyl Violet S4B
Chrome F	Dianil Azarine	Methyl Alkali Blue
Pontachrome Black K	Diamine Blue BX	Rose Bengale
Solochrome Black A	Columbia Blue G	Induline Soluble
Resorcin Yellow	Chicago Blue R	Nigrosine WSB
Naphthyl Blue Black N	Eboli Blue 6A	Anthraquinone Green GX
Naphthol Black 6B	Newport Direct Blue	Alizarin Blue Black B
Brilliant Croceine 9B	Chicago Blue RW	Anthraquinone Blue SR
Diamine Blue 6G	Direct Deep Black E extra	Acid Blue GR conc.
Naphthol Black 3B	Direct Orange G	

Pigmentation of the crystals due to a mechanical enclosure of dye crystals or particles, or to the presence of negative crystal cavities containing dye solution was not observed.

*Anomalous Pleochroism.* Examination in polarized light of the dye-tinted crystals described above revealed numerous instances of anomalous pleochroism. A list of the dyes affording this effect, together with a statement of the optic orientation, is given in Table 4. The occurrence of anomalous pleochroism in dye-tinted crystals was first described by de Senarmont, in 1854, and was later studied in detail by Gaubert (8) and Buckley (25). The pleochroism arises from the oriented enclosure of dye molecules or of dye crystals, which impress their own optical behavior on the host crystal. Anomalous pleochroism is also found in natural crystals that contain a foreign pigmentsing substance. The natural crystals of NaF (*villiaumite*) are deep carmine in color and pleochroic, but these effects are due to radioactivity.<sup>a</sup>

<sup>a</sup> Villiaumite occurs in nepheline syenite pegmatite as anhedral masses with marked dichroism in carmine red (*o*) and gold (*e*). The crystals are anomalously weakly birefringent, with extinction parallel to rows of negative crystal cavities or inclusions (arranged parallel {100}?). X-ray examination proves the crystals to be identical with artificial NaF (Barth, T., and Lunde: *Centr. Min.*, 57, 1927 A).



TABLE 4. DYES PLEOCHROIC IN NaF

Dye	Relation of [100] to vibration direction	
	Parallel	Perpendicular
Croceine Orange*	yellow	golden-yellow
Bordeaux B*	yellow-rose	rose
Diamine Blue 6G	lavender	blue
Napthol Black 3B	violet	light violet
Pontamine Fast Pink BL	yellow	red-orange
Dianil Azarine	lavender	blue
Diamine Blue BX	lavender	blue
Columbia Blue G	lavender	blue
Eboli Blue 6A*	light purple	purple
Induline Soluble*	light purple	purple
Anthraquinone Green GX	light green	dark green
Anthraquinone Blue SR	light blue	blue

\* In solutions made faintly acid with HCl.

#### EFFECT OF DYES ON LiF

None of the 39 dyes investigated with LiF effected variation from the ordinary {100} habit of this substance. With but few exceptions skeletal cubes, similar to Figs. 1 and 2 admixed with normal cubes, were obtained from the dye crystallizations. A few dyes, among which may be mentioned Orange I, Solochrome Black, and Croceine Orange, interfered markedly with the crystallization and tended to produce extraordinarily delicate lattice-like growths and needle crystals. The latter two dyes effected habit variation in NaF.

*Coloration. Anomalous Pleochroism and Birefringence.* Anomalous pleochroism was noted only with Diamine Blue BX. A number of other dyes were adsorbed by {100}, and afforded tinted cubes and skeletal cubes, but without pleochroism. These dyes are listed in Table 5. Coloration and pleochroism were difficult to recognize with LiF because of the small size of the crystals formed by this substance. Several dyes, notably Newport Direct Blue, Solochrome Black, Diamine Blue 6G, and Napthol Black 3B, when present in relatively high concentrations caused the formation of minute, deeply tinted, irregular granules of LiF.

TABLE 5. DYES ADSORBED BY {100} OF LiF

Napthol Yellow S	Diamine Blue 6G	Azo Blue
Palatine Scarlet	Napthol Black 3B	Newport Direct Blue 3B
Orange III	Congo Red	Acid Violet 4BN
Resorcin Yellow	Diamine Blue BX	Formyl Violet S4B
Solochrome Black	Acid Anthracene	Anthraquinone Green GX
Croceine Scarlet 3B	Benzopurpurin 4B	

Strong anomalous birefringence was found to be produced in LiF by the colloidal dyes Congo Red and Benzopurpurin 4B. The dyes tinted the crystals deep red. The birefringence was developed in the growth sectors beneath the {100} faces, with extinction parallel to the cube edges.

#### EFFECT OF DYES ON NaCl

None of the 62 dyes investigated with this substance was found to effect habit variation from the ordinary cubical habit. A number of dyes, however, interfered with the crystallization. Here may be mentioned Chromotrope 2R, Acid Fuchsin, Fast Yellow G, Brilliant Croceine 9B and Methylene Violet 2RA. Several of these dyes effected variation in habit with other halides.

The skeletal growths produced in NaF and LiF by dyes were not observed with NaCl. Hopper-shaped crystals, however, often formed at the surface of the evaporating solution.

The cubes of NaCl obtained in the crystallizations quite generally were opaque and possessed little mechanical strength. These characters appeared to be due to the existence of minute elongated cavities in the crystals disposed parallel to the cube edges, probably resulting from a tendency for hopper-growth. For this reason the possibility could not be excluded that the color of the crystals was due to the mechanical enclosure of dye-tinted mother liquid.

#### EFFECT OF DYES ON KCl

The crystallizations of this substance were made on a microscope slide, as previously described. Five of the 56 dyes investigated were found to produce a variation to octahedral from the ordinary cubical habit. These dyes were Brilliant Croceine 9B, Superchrome Yellow RN, Naphthol Black 6B, Pontamine Blue BBF and Pontamine Yellow XSG. A doubtful effect was noted with Chromotrope 2R and Alizarin Blue Black B, and it is possible that other instances went unrecognized.<sup>a</sup>

The super-saturation effects noted with NaF, LiF and NaCl were relatively marked with KCl, KBr and KI. Brilliant Yellow S, Chrome 2R and the habit-varying dyes previously named were quite effective in this

<sup>a</sup> In observing crystallizations of alkali halides extreme care should be taken to distinguish between true modifying faces and attachment faces. The latter are single faces developed on the cubes that form at the surface of the solution, and represent the surface by which the crystals hung at the liquid interface. The face invariably approximates in position to {111} and often is perfectly plane and lustrous. Such attachment faces on NaCl and other halides were erroneously described by Retgers, J. W. (*Zeits. anorg. Chem.*, **9**, 267, 1892) as true modifying faces, under the name "one-corner modification." When such crystals sink and rest upon the slide they closely simulate octahedra or cubo-octahedra when viewed directly from above.

respect with KCl. The effect, however, appeared to be produced by any soluble dye if present in sufficiently large concentration. Marked supersaturation was observed even in cold KCl solutions.

*Rate of Growth Effects.* The effectiveness of the dyes in producing change in habit varied with the rate of growth of the KCl crystals. Only cubes were formed during the first stages of cooling of the dye-containing solution. Under these conditions the crystals grow rapidly, as a consequence of the marked temperature rate of change of solubility. As the solution cools and the crystals grow more slowly, octahedral faces appear on the cubes. Finally, under conditions of very slow growth by evaporation at room temperature, complete octahedra are formed. The effect of rapid growth in counter-acting the habit-varying influence of a cosolute was early recognized by Beudant (1818) and by Necker (1837), and many additional instances are to be found in more recent literature. The variation in habit with rate of growth of crystals formed from pure solution was first remarked in 1669 by Robert Boyle, who also noted the effect of impurities in causing habit variation.

#### EFFECT OF DYES ON KBr

No well-defined instances of habit variation were found among the 20 dyes investigated. Brilliant Croceine 9B interfered with the crystallization and in one experiment afforded irregular cubical crystals with small unequally developed {111} faces. Efforts to verify this observation were unsuccessful.

#### EFFECT OF DYES ON KI

Of the 16 dyes investigated only Acid Fuchsin and Brilliant Yellow S effected variation in habit. Both dyes caused the development of cubo-octahedra and octahedra under conditions of slow growth. These dyes were also found to interfere with the crystallization of other of the halides, but without changing the habit.

#### DISCUSSION

##### DYE ADSORPTION THEORY OF BUCKLEY

Buckley has concluded (3, 4) that the mode of attachment of dyes and of foreign inorganic ions of the  $RO_x$ -type to growing crystals of oxy-salts is identical in nature. The seat of the attaching power in the dye molecule is located in the substituent  $SO_3Na$  groups. The oxygen-triangles in these groups appear to substitute for oxygen-triangles of similar size and shape in the oxy-salt, in the same manner that tetrahedral inorganic anions of the  $RO_x$ -type substitute for  $SO_4^{=}$  in  $K_2SO_4$  crystals.



The substitution, or adsorption, of the polar groups in this way serves to anchor the rest of the dye nucleus, which is inert in itself, to the adsorbing surface. Because of the great bulk of the dye molecule, the habit-varying effect may be 50 to 100 times that of an inorganic ion. Other factors which have been found to influence the adsorption include the number of the substituent polar groups and their position on the dye nucleus, the composition of the group itself, and the *pH* of the solution.

It is not possible to explain the adsorption of dyes by crystals of the NaCl-type alkali halides on this basis. An attachment of dye by the substitution of sulphonate groups into the halide structure is not feasible, for structural reasons. The halide anions differ in charge and, with the exception of  $F^-$ , in size from the oxygen atoms of the sulphonate groups. Further, anion configurations compatible in shape and dimensions with the oxygen-triangles of the  $SO_3Na$  groups do not exist in the halides. While a triangular configuration is found in (111) of the halides, the inter-ionic distances are too great to permit a substitutional meshing by the oxygen-triangles of the dyes. In (111) planes the triangle-side for LiF is 2.84 Å, for NaF 3.26 and the values increase in the series  $Li^+ \rightarrow Rb^+$  and  $F^- \rightarrow I^-$  to 4.98 in KI and 5.18 in RbI. These values compare with a probable value of 2.6 Å or less for the oxygen-triangles of the  $SO_3Na$  groups.

The adsorption of dyes by precipitated AgCl (a NaCl-type substance) is viewed by Kolthoff (9) as an exchange adsorption between the dye ions and crystal ions of the same sign immediately adjacent to the surface of the AgCl crystal. On the other hand, Verwey (10) views dye adsorption by precipitated AgCl as involving an exchange between the dye ions and counter-ions in the outer, diffuse, part of the double-layer enveloping the AgCl crystals. Neither mechanism appears adequate to account for the habit variation in the alkali halides. While the adsorption of dye in either of these two ways would slow the normal growth velocity of the adsorbing surface, and thus satisfy the essential condition for habit variation, there is no reason to suppose that the dye should be adsorbed on crystal faces other than those of the normal {100} habit. A mechanism of the type described by Verwey, in which the dye is loosely held adjacent to the crystal surface, seems very improbable in the present instance. The occurrence of coloration and, in particular, of anomalous pleochroism in the halide crystals indicates that the dye has in some way been directly attached to the crystal surface.

It is interesting to note that two hydroxyl-containing dyes, Solochrome Black and Haematoxylin (Fig. 3), effect habit variation to octahedral in NaF. Possibly the effect of these dyes is due to the substitutional attachment of the OH groups for F ions in the NaF, analogous to the sub-

stitution of  $\text{SO}_3\text{Na}$  groups into oxysalts. It may also be noted that sodium citrate is extremely effective in producing variation to octahedral in  $\text{NaF}$ . The citrate anion itself possesses substituent  $\text{OH}$  groups, to which the adsorption may be owing.

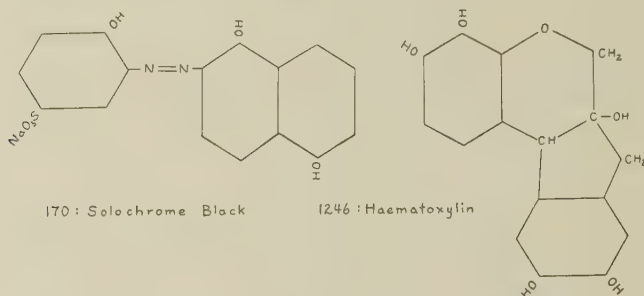


FIG. 3

The other effective dyes do not appear to possess any common character, either in size, structure or in the kind and relative position of their polar groups, and the source of their habit-varying power is obscure.

#### DYE ADSORPTION THEORY OF FRANCE

France and co-workers have developed the idea that "if any given substance is going to adsorb a foreign substance the adsorption will take place at those faces having the strongest fields of force" (11). It is also held that crystals growing from pure solution should develop faces that have the least field of force. A test may be made of this theory using the same criterion accepted by France for the identification of supposed high field forms, namely, a geometrical distinction between planes populated solely by ions of the same sign (high field planes) and planes populated by both positive and negative ions (low field planes).

In substances of the  $\text{NaCl}$  structural-type the theory requires (111) to be the most strongly adsorbing form, and (100) and (110) to be weakly or non-adsorbing.<sup>a</sup> Survey of the instances of dye adsorption by crystals of this type shows, however, that adsorption by (111) is the exception and not the rule. Thus of the 59 instances of dye adsorption by  $\text{NaF}$  and  $\text{LiF}$ , as evidenced by habit variation, pleochroism or coloration, 55 are of adsorption by (100) planes and only 4 by (111) planes. A similar behavior is found with  $\text{AgCl}$ . Reinders (12) found that of 38 dyes, 15 were not taken up by the  $\text{AgCl}$  crystals, 5 produced dendritic growths of unknown habit, and 18 were taken up but without change from the normal (cubo-octahedral) habit. Gaubert, moreover, states from his own observations

<sup>a</sup> In this structure-type all planes with  $h$ ,  $k$  and  $l$  odd contain solely ions of the same sign.

(13) with AgCl and AgBr that the dye is selectively adsorbed by the {100} faces.

Numerous instances of the adsorption of inorganic cosolutes by the supposedly low field planes are also known. A list of such instances is given in Table 6. Doubtlessly most instances of the adsorption of colorless cosolutes by (100) in the alkali halides go unnoticed, since such adsorption is not made apparent by habit variation and must be shown by special methods.

TABLE 6. SELECTIVE ADSORPTION BY "NEUTRAL PLANES" IN NaCl-TYPE SUBSTANCES

Crystallized Substance	Cosolute	Adsorption Habit	Authority
NaCl	HgCl <sub>2</sub>	(110)	Gille and Spangenberg; Royer; Orloff
NaCl	AlCl <sub>3</sub>	(110)+(100)+(111)	Gille and Spangenberg
NaCl	SbCl <sub>3</sub>	(110)+(100)+(111)	Orloff
NaCl	Ba(SbO) tartrate	(110), (210), (211), (332), etc.	Traube; Orloff
NaCl	glycocoll	(210), (310), etc.	Orloff
NaCl	urine	(543)?	Knop
NaCl	Bi <sup>+3</sup>	(110)	Yamamoto
NaCl	Cd <sup>+2</sup>	(110)	Yamamoto
NaCl	Pb <sup>+2</sup>	(100)	Gibbs and Clayton; Hahn; and others
NaCl	propionic acid	(210)+(100)+(111)	Groth
KCl	urea	(100)	France
KCl	urine	(411)	Knop
KCl	wormwood extract	(211)	Claasen
KCl	Bi <sup>+3</sup>	(110), (210)	Yamamoto
KCl	Pb <sup>+2</sup>	(100)	Hahn
KBr	PbBr <sub>2</sub>	(110)	Retgers
KBr	urea	(100)	France
NaF	H <sub>3</sub> BO <sub>3</sub>	(110)	Frondel
RbCl	Ti <sup>+3</sup>	(110)	Yamamoto
RbCl	ZrO <sup>+2</sup>	(210)?, (111)	Yamamoto

Several objections of a more general nature to the theory of France may now be pointed out. The theory itself is based on the fundamental assumption that there are differences in surface energy between faces of crystals which are significant with regard to crystal growth and adsorption. This assumption, however, is subject to a restriction which denies the application of the theory to the growth and adsorptive behaviors of macroscopic crystals. As shown by Willard Gibbs (14), sub-microscopic crystals are in equilibrium with their solution when their bounding faces



are those of minimum surface energy. This applies, however, only to crystals below about 0.001 mm. in size, i.e., to crystals in the size range where the surface area, which is the capacity factor of surface energy, is relatively greatly developed. With macroscopic crystals the differences in surface energy between different crystal faces are practically equal to zero and are without influence on the habit development (15). The restriction was realized by Gibbs but not by Curie (16), who later independently expressed a similar theory. The size above which surface energy differences between faces become negligible was estimated in this connection by Berthoud (17), from the relation between particle size and solubility found by Hulett (18).

Experimental verification of this qualification in point of size is found in the observed equilibrium behavior of crystal spheres and polyhedra in saturated solutions (19). Cottrell (20) also concluded from experiments on the behavior of NaCl octahedra in saturated NaCl solutions that the Gibbs relation did not hold for macroscopic crystals. The theory of France fails for this reason. Explanation of the adsorptive behavior of macro-crystals—which itself is largely at variance with the proposed relation, accepting the criteria for high field faces given by France—must be sought in some other direction.

The growth mechanism of macroscopic ionic crystals of the NaCl-type has been semi-quantitatively analyzed by Kossel (21) and by Stranski (22), from consideration of the energy changes accompanying the removal from solution, dehydration and ordered packing of ions into the structure. The general point of view of France cannot be reconciled with this work, in which growth and adsorption are related directly to the geometrical situation of the surface ions and the crystal chemistry of the substances involved, rather than to areal surface energies.

France also concludes (23) from an observed identity of cell dimensions of pure and of dye-tinted crystals that the dye is adsorbed interstitially. This conclusion is unjustified. The identification of a solid solution effect as substitutional, interstitial or omission, and the distinction of these from a purely mechanical enclosure of foreign materials, requires the application of criteria (24) beyond the measurement of cell dimensions. Further, variation in cell dimensions in itself is not a necessary concomitant of any type of solid solution.

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# THE RAPAKIVI OF HEAD HARBOR ISLAND, MAINE

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## ABSTRACT

The granite of Head Harbor Island, Maine, a facies of the normal granite of Jonesboro, has the textural peculiarities of a typical rapakivi, including coarse grain and large rounded potash feldspar phenocrysts mantled by oligoclase. The occurrence and microscopic appearance of the rock suggest that it is of magmatic origin and not a product of granitization.

An examination of the normative feldspar content of 34 analyzed rapakivis and genetically related rocks indicates that these are, with few exceptions, represented by points lying in the plagioclase field of Bowen's equilibrium diagram for the system *or-ab-an*, in contrast to many granitized sediments whose projection points lie in the orthoclase field. This fact is believed to support the hypothesis that most rapakivis are of magmatic origin. The peculiar rapakivi texture occurs most commonly in rocks whose projection points lie on or near the boundary between the two fields, a circumstance to which the large size of the phenocrysts is thought to be related.

Although some of the older hypotheses concerning the origin of the oligoclase mantles are not discarded, it is suggested that these mantles may be due to a change in the position of the orthoclase-plagioclase field boundary.

## DEFINITIONS

Among the earliest descriptions of rapakivi is that published by Sederholm in 1891. In 1928 the same writer defined the rock as a granite containing large rounded phenocrysts, or ovoids as he called them, of potash feldspar mantled by sodic plagioclase. Wahl (1925) has applied the term *pyterlite* to rapakivi-like rocks in which the ovoids are not mantled. These are so closely related to rapakivi in general appearance and in mineralogical composition that they may be considered as a variety of this species. While several investigators have applied the term rapakivi to rocks associated with, related to, or in some respect similar to the rapakivi in the narrower sense, the term will be applied in this article only to rocks actually containing conspicuous large rounded crystals of potash feldspar mantled by sodic plagioclase.

## DESCRIPTION

On Head Harbor Island, near Jonesport, mapped in part on the Columbia Falls sheet and in part on the Great Wass Island sheet of the U. S. Geological Survey, is a rapakivi whose general appearance and mineralogical composition are so similar to that of the granite of Jonesboro which outcrops farther north in the same quadrangle and on nearby islands, that it seems to be unquestionably a facies of this rock.

The typical granite of Jonesboro, an older analysis of which is given below, consists essentially of perthitic orthoclase, oligoclase, quartz and

biotite. With the exception of a few idiomorphic, apparently partially resorbed oligoclase phenocrysts 5 to 10 mm. long, the individuals of the various minerals are generally all about the same size, and have a diameter of several millimeters in typical specimens. Perthite occasionally exhibits idiomorphism, and in some outcrops is commonly, although not invariably, mantled by orthoclase. Neither the typical granite of Jonesboro nor its rapakivi facies show notable evidence of having undergone a tectonic disturbance, and they were probably intruded after the folding of the Silurian volcanics and sediments which outcrop in the area. Two of the lower members of this series, a quartz latite and a rhyolite, contain large amounts of secondary quartz, possibly a metamorphic effect of the granite, but the intercalated and overlying shales show no obvious effects of metamorphism.

The Head Harbor Island rapakivi differs from the typical granite of Jonesboro in that it is coarser grained and contains the large rounded phenocrysts (ovoids) of potash feldspar mantled by oligoclase which are typical of rapakivi. Professor Sederholm, who very kindly examined the writer's specimens in 1930, stated that they were similar to certain Finnish rapakivis. The Maine occurrence differs from the classical rapakivis of Finland in that the ovoids are less abundant and do not exceed about 2 cm. in length, whereas those of many Finnish rapakivis have a length of 8 cm. or more, 4 cm. being an average length. In the composition of the plagioclase mantles ( $ab_{78}an_{19}or_3$ ), the Head Harbor Island rapakivi conforms closely to the Finnish type, except that the former contain somewhat less potash than those of Finnish rapakivis for which analyses are available. The potash feldspar ovoids of the Head Harbor Island rock are richer in soda than many of those of the Finnish rapakivi. Analyses of the perthite and of the oligoclase are given in Table 1. Like the normal granite of Jonesboro, the rapakivi facies contains a few large partially resorbed individuals of oligoclase which are smaller than the perthite ovoids but larger than minerals of the groundmass which are generally several millimeters in diameter. The groundmass consists of perthite, oligoclase and biotite.

Within the perthite phenocrysts, in a zone just beneath the surface, are a number of very small idiomorphic crystals of oligoclase, many of which have at least approximately the same orientation. As may be seen in Fig. 1, the (010) plane of these is roughly perpendicular to those of the mantle oligoclase and of the orthoclase of the ovoids. Small oligoclase individuals within the ovoids have also been observed in a few of the Finnish rapakivi (Backlund 1938b). The deposition of the oligoclase mantles was preceded or accompanied by some resorption of the orthoclase ovoids, as may be seen in Fig. 1. These mantles are composed of a



FIG. 1

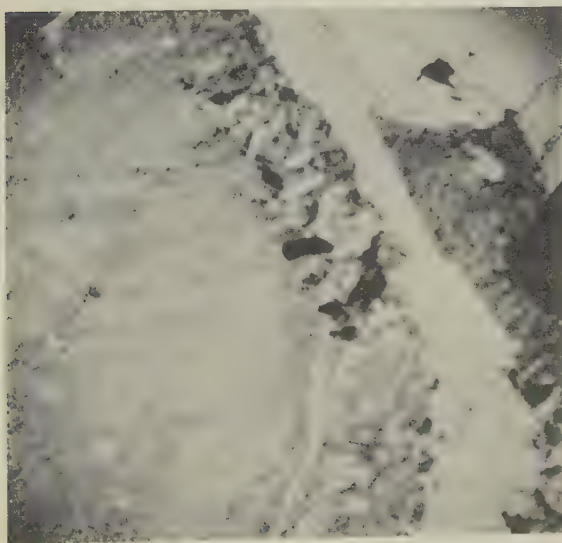


FIG. 2

FIG. 1. A portion of a perthitic ovoid with mantle and inclusions of oligoclase. The section is approximately parallel to the (100) plane of the orthoclase. The trace of the twinning lamellae of the mantle oligoclase is approximately parallel to that of the composition plane of the Carlsbad twins of the orthoclase. Crossed Nicols.  $\times 22$ .

FIG. 2. The same ovoid. Quartz veinlets and inclusions appear as white spots within the feldspar. A small part of the Carlsbad composition plane appears indistinctly in the lower left-hand corner. Ordinary light.  $\times 14$ .



number of sub-parallel individuals through which the twinning lamellae are not continuous. In this feature, the Maine rapakivi is similar to certain of the Finnish ones, according to a description published by Popoff in 1928. At one corner of the section shown in Fig. 1 may be seen a portion of an outer rim of perthite which does not however completely mantle the phenocryst. While numerous successive oscillations of this sort are common in some of the Finnish rapakivi, they are rather rare in that of Head Harbor Island and are never well developed.

Scattered throughout the phenocrysts, chiefly in the potash feldspar core but also to some extent in the oligoclase mantles, are small masses of



FIG. 3. Quartz veinlet in a perthite ovoid. Ordinary light.  $\times 74$ .

quartz comprising roughly 2 per cent of the volume of the feldspar. Most of these are elongated and have irregular, in part concave, surfaces. They are generally less than 0.5 mm. long, the largest having a length of about 1 mm. A number of them appear as small white spots in Fig. 2 and one is shown highly magnified in Fig. 3. They appear to be replacement veinlets. Popoff (1928) described similar veinlets which he considered eutectic intergrowths with the feldspar. Rounded quartz grains having a diameter of 0.01 mm. or less are present in a zone 0.02 to 0.05 mm. wide, located within the potash feldspar ovoid approximately 0.7 mm. from its periphery, to which the zone is roughly parallel. (Figs. 1 and 2.) These appear to be inclusions which were partially resorbed before inclusion occurred. The parallelism between this zone and the surface of the ovoids indicates that the rounded form of the ovoids was acquired before the growth was complete, and that it is not merely a result of partial resorption at a final stage in their development.

Zircon and apatite are rare accessories in the normal granite as well as in the rapakivi.

TABLE 1. CHEMICAL ANALYSES

	1	2	3		Norms	
					Marsh- field granite	Rapakivi Hd. Harb. Is. (est.)
SiO <sub>2</sub>	72.97	65.38	63.08			
TiO <sub>2</sub>	n.d.	none	none			
Al <sub>2</sub> O <sub>3</sub>	14.63	18.96	22.90	qu	28.72	27
Fe <sub>2</sub> O <sub>3</sub>	n.d.	0.48	0.46	or	31.18	28
FeO	1.73	none	n.d.	ab	27.75	36
CaO	1.48	0.18	3.80	an	7.33*	6
SrO	n.d.	none	n.d.	C	0.80	
MgO	0.27	0.12	trace	hy	3.85	3
MnO	0.10	none	none	or:ab:an=	47:42:11	40:52:8
K <sub>2</sub> O	5.18	10.74	0.56		Optical Data	
Na <sub>2</sub> O	3.28	3.64	8.80		$\beta(\pm 0.003)$	Max. ext. Est. an
BaO	n.d.	0.06	n.d.			$\perp 010$ %†
S	0.03	n.d.	n.d.	orthoclase	1.525	—
CO <sub>2</sub>	none	n.d.	n.d.	perthitic albite	1.532	13° 5
H <sub>2</sub> O	n.d.	0.44	0.32	oligoclase	1.540	3° 16
	99.67	100.00	99.92			

1. Marshfield granite, Booth Bros. Jonesboro Quarry, quoted from T. N. Dale (1907). Analysts, Ricketts and Banks.

2. Perthite ovoids from rapakivi of Head Harbor Island. Analyst, F. A. Gonyer.

3. Oligoclase of rapakivi of Head Harbor Island. Since the oligoclase of the ground mass and of the mantles had the same optical properties, no effort was made to separate them. Analyst, F. A. Gonyer.

\* This value may be too high, since P<sub>2</sub>O<sub>5</sub> and F were not determined.

† Corresponding to the optical data as given in Goranson's tables (1926).

In column (1) below, are given the mineral components of the perthite ovoids, in (2) those of the oligoclase, in (3) the estimated total minerals of the rapakivi, in (4) the estimated total minerals of the analyzed Marshfield granite, as calculated on the basis of the analysis and the minerals invariably present in the Marshfield granite, and in (5) the essential minerals of a typical specimen of the Marshfield granite from the Booth Brothers' Jonesboro Quarry, as estimated from a thin section. All quantities are given in weight per cent.

	(1)	(2)	(3)	(4)		(5)
quartz			27	37	quartz	35
orthoclase	62.4	3.1	26	23	perthite	40
albite	36.0	78.4	36	27	plagioclase { albite	18
anorthite	1.6	18.5	6	6	{ anorthite	2
biotite			5	7	biotite + chlorite	5

#### COMPOSITION AND ORIGIN OF THE RAPAKIVI GROUP

Until recently the rapakivi granites of Finland, the classical land of granitization, have been considered true igneous rocks. In 1938(b)

Backlund published for the first time in English the hypothesis that they have originated by the granitization of sandstones. The enunciation of this hypothesis has stimulated a lively controversy (Eckermann 1937, Backlund 1938a) which students of the problem may follow with profit and interest. So many convincing arguments are presented by both sides that the question immediately arises as to whether two or more different processes may not be capable of producing the rapakivi texture, with the result that each individual case must be examined on its own merits. In the Head Harbor Island occurrence, the writer found no evidence that the rapakivi is not of normal igneous origin. There is, for instance, no transition whatsoever between the typical granite and the practically unaltered older shales and volcanic rocks of the area. Moreover, the different orientations of the oligoclase of the mantles and of the inclusions within the perthite ovoids suggest two different origins for the two forms, and are not readily reconciled with the hypothesis of granitization.

The chemical composition of the rapakivi group as a whole, including the related rocks, offers statistical evidence in favor of an igneous origin. Conversely, if the rapakivis are true igneous rocks, the chemical composition of the group throws an interesting light on the origin of their texture. In Fig. 4 are shown the normative feldspars, recalculated to 100 per cent, of 34 fresh rapakivis and related granites (Carstens 1925; Eskola 1928, 1930; Hackmann 1934; Kanerva 1928; Laitakari 1928; Wahl 1925) including those of the one known American occurrence and of the normal granite of which this rapakivi is a facies. (Although there are about fifty superior analyses of fresh so-called rapakivis and related rocks, some of these, like the excellent and complete analyses and descriptions published by v. Eckermann (1936) refer to groups of rocks which include no true rapakivi, and others are not accompanied by descriptions which permit their classification as true rapakivi or as merely related granites. Such analyses are not represented in the diagram.) The true rapakivis are indicated in the figure by dots, while the related rocks are shown by circles. The curve is a part of the Bowen (1928) field boundary for the system *or-ab-an*, the exact location being based on evidence described by the present writer (Doggett, 1929).

It is a striking fact that many points representing the composition of rapakivi and related rocks lie on the field boundary and in the plagioclase field, but almost none in the orthoclase field. This limited range of composition would probably be a necessary feature of a group of unaltered rocks of igneous origin, but there is no apparent reason why their composition should be thus limited if they are all the products of granitization of sediments, many such rocks, as well as an extremely large number



of granites of unknown origin being represented by points in the orthoclase field (Terzaghi 1935).

Of the 14 points representing true rapakivis in Fig. 4, 8 lie on or very near the field boundary. Over half the points lying on or near this line represent true rapakivis, while less than one third of those lying well within the orthoclase field represent such rocks. Even among the large number of rocks whose analyses are given in Washington's tables (1917) there are almost none other than rapakivis, either among the coarse or

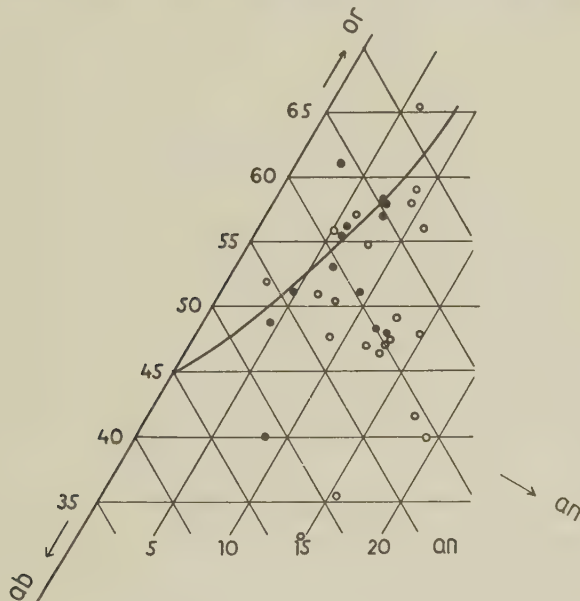


FIG. 4. The normative feldspar content of some rapakivis and related rocks plotted on a part of the hypothetical equilibrium diagram for the system *or-ab-an* (Bowen, 1928; Terzaghi 1929). Rapakivis and pyterlites are shown by dots, related rocks not having the rapakivi or pyterlite structure by circles.

the fine-grained rocks, whose composition corresponds to that of the rapakivis lying on the field boundary between points representing 54 and 58 *or*. Two interpretations of these facts occur to the writer. One is that the rapakivi composition is not attained by true magmas, and that the rapakivis are, therefore, as Backlund believes, of non-magmatic origin. On the other hand, if they are of magmatic origin, the rarity of rocks having the typical composition but not the texture of rapakivi suggest that this texture is a function of the composition. That composition is not the only factor involved is indicated by the fact that some rapakivis, includ-

ing that of Head Harbor Island, do not have the typical rapakivi composition corresponding to points lying on the field boundary.

Among the many problems which arise in connection with the origin of the rapakivi texture, two are particularly interesting. The first of these involves the presence of potash feldspar phenocrysts in rocks whose bulk composition lies in the plagioclase field. Although there are many non-rapakivis which present this same problem, the consideration of these would transgress the limits of this article. However, much of the discussion of the origin of the rapakivi ovoids would apply equally well to the potash feldspar phenocrysts of other rocks. The second aspect of the problem is the origin of the mantle of sodic plagioclase surrounding the perthitic ovoids.

Many investigators have assumed that idiomorphism and large size of the individuals of any given mineral species indicate that that mineral was the first or among the first to crystallize from the magma. However, the course of differentiation—assuming an igneous origin—of several Finnish rapakivi series was such that the younger members of each series are richer in potash than the older members of the same series (Backlund 1938b). This indicates early separation not of orthoclase but of plagioclase, which is to be expected from the fact that the projection points of these rocks lie in the plagioclase field of the equilibrium diagram. It is therefore apparent that some cause, other than early crystallization, of the large size and idiomorphism of the potash feldspar individuals must be sought.

As will be shown in the following paragraphs, a consideration of the relative amounts of the two feldspars, and the relative rates at which the individual crystals probably grew, if they started to develop at the same time, indicates that a few large and probably idiomorphic potash feldspar individuals may develop simultaneously with a great number of smaller plagioclase crystals. Under certain conditions, it would appear that the potash feldspar individuals may develop a relatively large size even though they begin to crystallize later.

According to two sets of analyses given by Wahl (1925) the rapakivi whose projection points lie on the field boundary at about 55 *or* may contain potash feldspar ovoids consisting of 65 to 75 per cent orthoclase-molecule and 25 to 35 per cent highly sodic plagioclase, while the plagioclase individuals contain less than 9 per cent *or*. Assuming that the present bulk composition of the perthitic ovoids represents their original composition, there was 2.5 to 5 times as much potash feldspar substance (*or*+*ab*) in the magma as there was plagioclase. Hence a layer of liquid of infinitesimal thickness on each face of a crystal growing in such a magma contains 2.5 to 5 times as much potash feldspar substance as

plagioclase, which must crystallize in response to the loss of a given heat quantity. If diffusion is able to keep pace with crystallization, the linear growth of the potash feldspar crystals may thus be 2.5 to 5 times as rapid as that of the plagioclase. While the potash feldspar crystals are growing rapidly and sweeping in the material from a relatively large volume of liquid, the plagioclase individuals grow slowly and derive their material from a correspondingly small volume. As a result, the liquid not immediately adjacent to plagioclase crystals is likely to become saturated with plagioclase, so that new centers of crystallization may be established. Thus the smaller quantity of plagioclase is divided among many crystals while the larger quantity of potash feldspar substance (*or+ab*) is divided among few crystals. If the ratio of their rates of lineal growth remains between 2.5 and 5 throughout the period of development, the ratio of their individual volumes will be between 15 and 125, assuming a roughly equidimensional habit. The large size and relatively rapid development (compared to the plagioclase) of the potash feldspar may account for the rounded outlines of typical ovoids of rapakivi.

If, on the other hand, the magma is rapidly cooled, a large number of crystals of both sorts may be developed, with the result that none of these can attain either relatively or absolutely great size. That slow cooling is, in fact, generally a necessary condition for the development of the rapakivi texture is indicated by the circumstance that this texture is very rare in fine-grained rocks and that the contact facies of some rapakivi masses lacks the rapakivi texture. (See for instance Laitakari's (1928) description of the Vakkära granite.)

According to this hypothesis of the origin of potash feldspar phenocrysts, a large amount of solid solution of plagioclase (chiefly albite) in the potash-feldspar solid phase, accompanied by little or no solid solution of orthoclase molecules in the plagioclase phase favors the development of potash feldspar phenocrysts. This offers a clue to the fact that the rapakivi texture is more likely to be present in rocks containing a moderately calcic plagioclase than in those containing a highly sodic one, since the potash feldspar molecule enters only slightly into solid solution with a plagioclase which is even moderately calcic, whereas it may be present in large amounts in an alkaline plagioclase (Mäkinen 1917). The soda content of orthoclase apparently does not necessarily vary greatly with the composition of the magma.

We may now consider the case of rapakivi texture in rocks whose feldspar content is represented by points not lying near the field boundary. Under normal conditions, the plagioclase crystals may have attained a considerable size before the potash feldspar begins to crystallize, with the result that the latter will not be able to overtake the former in size. If



however, the magma is injected in such a way that the first stage of the cooling is accomplished rapidly, giving rise to many small plagioclase individuals, while the latter part of the cooling (after the orthoclase begins to crystallize), progresses slowly, the potash feldspar may be concentrated in a few large individuals. If the composition of the potash feldspar is very near that of the melt from which it is crystallizing, while that of the plagioclase is very different, the ratio of potash feldspar to plagioclase will be high and the development of large idiomorphic and possibly rounded potash feldspar individuals will of course be favored. Assuming that the composition of the Head Harbor Island rapakivi magma "arrived" at the field boundary at a point corresponding to about 52 *or*, the ratio of potash feldspar substance (*or*+*ab*) to plagioclase in the remaining melt would have been about 6.8, a high ratio which must have contributed to the development of the large size of the ovoids.

The second aspect of the problem of the rapakivi texture is concerned with the origin of the oligoclase mantles which alternate in some cases with perthite mantles. In 1928 Sederholm gave an excellent summary (pp. 88-89) of the various hypotheses concerning their origin which had been proposed at that time.

Among the most interesting of the older hypotheses is that of Vogt (1906) who suggested that the oligoclase and perthite mantles of the ovoids may be due to an oscillation of the composition of the magma about the "eutectic" (field boundary), first the oligoclase becoming supersaturated and then the potash feldspar. However, the development of a state of super-saturation in the entire magma with respect to components present in the crystalline state seems to call for a special explanation, and it appears to the writer more likely that the field boundary may have oscillated about the projection point of the magma than that the composition of the magma oscillated about that corresponding to the field boundary. A possible cause of such a change in the position of the field boundary will be discussed below.

A somewhat similar hypothesis proposed by Sederholm (1928) obviates the difficulty just mentioned. He postulated that a limited zone immediately surrounding the potash feldspar ovoids may have become supersaturated with the components of the plagioclase, with the result that this material was deposited in place of the potash feldspar as a mantle about the ovoids. If, as the present writer believes, the potash feldspar ovoids grew more rapidly than did the individual plagioclase crystals, this mode of origin of the mantles would appear to be among the most plausible suggested.

On the other hand, it may be that a shift of equilibrium between the feldspars was responsible for the plagioclase mantles. Certain facts sug-

gest that the solubility of orthoclase in a magma may increase with increasing water content faster than that of sodic plagioclase (Terzaghi 1935). In other words, it appears that the field boundary may be shifted into the orthoclase field. If this is the case, an increase in the water content of the magma may cause the potash feldspar crystals to cease growing or even to be partially resorbed while oligoclase may be deposited in its place upon a further loss of heat. The quartz veinlets in the potash feldspar ovoids of the Maine rapakivi as well as in some others seem very clearly to represent replacement phenomena probably associated with a late stage of consolidation in which the remaining magma was rich in water, and they are thus in harmony with this hypothesis of the origin of the plagioclase shells.

Other things being equal, the upper limit set on the water content of a magma varies with the pressure on the gaseous phase with which the magma is more or less in equilibrium. If the cover is so pervious that the gas can escape readily, the water content of the magma may be reduced to a very low value. If the cover is impervious, the gas may develop a pressure equal to that exerted by the overlying column of rock, provided sufficient water is present in the magma. Thus very minor changes in the local conditions, such as the development or the closing of a few cracks in the overlying rocks, may be sufficient to cause variations in the water content of the magma. In this way, the position of the field boundary might be caused to oscillate, giving rise to the alternating deposition of plagioclase and of potash feldspar.

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# THE MORPHOLOGY OF COLUMBITE CRYSTALS

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## ABSTRACT

The space-group of columbite, obtained from the morphology, by the Donnay method (1938) is *Pman*, in a new setting ( $a:b:c=0.4023:1:0.3580$ ) chosen so as to comply with the convention  $c < a < b$ . In the same setting, the space-group found by x-ray methods (Sturdivant, 1930) is *Pcan*. The difference lies in the interpretation of the zone [100].

The classical law of Bravais does not agree with the observed facts as well as the generalized law (Donnay-Harker, 1937), which, although not perfect, is decidedly better.

## INTRODUCTION

Columbite,  $(\text{Fe,Mn})(\text{Nb,Ta})_2\text{O}_6$ , crystallizes in the orthorhombic system. It is of special interest on account of the anomalous zone of the  $(0kl)$  faces, which makes it impossible to reconcile the space-group determined from the morphology, with the space-group indicated by x-rays. In the first part of the paper the space-group is derived by the morphological method (Donnay, 1938,  $a\ b\ c$ ) and special reference is made to the anomalies. The second part is devoted to a comparison of the classical law of Bravais with the generalized law (Donnay-Harker, 1937) in order to determine which of the two conforms more closely to the observed facts.

## OBSERVATION DATA

V. Goldschmidt's axial elements and setting are adopted provisionally. His letters are also used throughout to denote the forms (*Atlas der Krystallformen*, 1913). Of the ninety figures given in Goldschmidt's *Atlas*, eighty-two were studied with a view to estimate the relative importance of the forms occurring on columbite crystals (eight figures lacking clarity were disregarded).

The cleavage forms,  $b\{010\}$ , rather distinct, and  $a\{100\}$ , less so, coincide with the dominant growth forms, a fact which, however, cannot be taken into account in estimating form importance (Donnay, 1938,  $c$ ). The importance of the forms is based primarily on the *frequency* of occurrence; their *size* is also taken into consideration, but is given less weight.

Several types of data are sought: (1) the relative importance of the forms for each crystal figured in the *Atlas*; (2) the relative importance of the forms for each locality; (3) the relative importance of the forms for the species as a whole. Tables 1 to 12 present the data on the first two points. In these tables the figure numbers in Goldschmidt's *Atlas* are indicated in the left hand column and are grouped according to locality.

TABLE 1  
Greenland

Fig. no. in Gdt.	Observer	Form	010 111 011 110 130 021 100 001 012 221 231 211 121 131 241 201 161 991 101 133 160 163 411 150 032																							
			<i>b</i>	<i>u</i>	<i>k</i>	<i>g</i>	<i>m</i>	<i>h</i>	<i>a</i>	<i>c</i>	<i>l</i>	<i>s</i>	$\pi$	$n$	$\beta$	$\theta$	<i>e</i>	<i>x</i>	<i>r</i>	<i>i</i>	$\alpha$	$\gamma$	$\sigma$	$\phi$	$z$	$z$
23	Des Cloizeaux		1	2	3	6	5		7	4	8	11	12	13	15	14	10			16						9
25	Breithaupt		1	3	8	2	4	10	6	7										9	11				4	
34	Schrauf		1	2	4	6	8		3		5	7														
35	Schrauf		1	3	3	2	8	6			3	10	6			9										
36	Schrauf		1	2	6	9	3	7	4	8	5	10	12		11											
37	Schrauf		1	4	7	3	5	2	6	8		10	9	11												
38	Schrauf		1	2	4	8	2	4		7	4		9	10	11	11		11								
39	Schrauf		1	2	3	4	5	6		7		8		9												
40	Schrauf		1	3	5	2	4	5			5	9	8	10		12	11									
41	Schrauf		1	3	5	7	6	9	4	2	8	10	13	15	12	16	11	14	17							
42	Schrauf		1	5	3	6	4	9	7	2	8	15	14	16	12	13	10	18	19	17	21		11	22	20	
43	Schrauf		1	3	2	6	4		5			8	10	7		9										
46	Schrauf		1	2	5	4	7	3	12		6	8	10	9	11											
47	Schrauf		1	3	2	7	4	6			5	8	10		11	14		13			9		12			
49	Schrauf		1	2	3	7	5		6	4																
50	Schrauf		1	2	3	8	9		10	4	7					6				5						

## EXPLANATION OF TABLES

In these tables each form is designated by Goldschmidt's letter and Miller indices ( $a:b:c=0.4023:1.0.3580$ ). The figure number in Goldschmidt's *Atlas* is given in the first column, the name of the observer in the second column. The number assigned to each form in the remaining columns is its rank in the sequence of decreasing importance for the forms of the figure considered. In each table the forms appear as column headings in the order of decreasing importance for the locality considered.

TABLE 2  
Bodenmais, Bavaria

Fig. no. in Gdt.	Form Observer	010 <i>b</i>	001 <i>c</i>	100 <i>a</i>	130 <i>m</i>	111 <i>u</i>	201 <i>e</i>	110 <i>g</i>	160 <i>y</i>	211 <i>n</i>	101 <i>i</i>	011 <i>k</i>	131 <i>o</i>	012 <i>l</i>
9	Dana	1	3	2	7	4	5	8	6	9				
11	Lévy	1	2	3	4	5	6							
12	Lévy	1	3	2		6		5			4			
13	Lévy	1	2	6	4	7	3	5						
14	Lévy	2	1	7	5			2			6	4		
16	Rose	1	2	3	3	6	5							
17	Rose	1	2	3		5	4	6	6					
28	Schrauf	1	2	3	4	6							5	7
30	Schrauf	1	2	3	7	4	5	8		6				
48	Schrauf	1	2	3	4		5							
56	Rath	1	2	3	6	7	5	4		8				

TABLE 3  
Ilmen Mountains

Fig. no. in Gdt.	Form Observer	010 <i>b</i>	100 <i>a</i>	111 <i>u</i>	201 <i>e</i>	130 <i>m</i>	110 <i>g</i>	150 <i>z</i>	121 $\beta$	131 <i>o</i>	001 <i>c</i>	160 <i>y</i>
20	Auerbach	1	2	3								
21	Auerbach	1	5	4	2	6	3					
22	Auerbach	1	5	4	2	6	3					
26	Nordenskjöld	1	5	3	2	6	4					
27	Nordenskjöld	1	2	3								
33	Schrauf	1	4	3	2	5	6					7
52	Maskelyne	1	3	6		5	7	4			2	
64	Kokscharow	1	3	5		2	4		6	7		
65	Kokscharow	1	3	4	6	2	5		7			
66	Kokscharow	1	4		3	2	5					

TABLE 4  
Haddam, Connecticut

Fig. no. in Gdt.	Observer	Form	010	100	001	130	110	111	160	201	211	101
			<i>b</i>	<i>a</i>	<i>c</i>	<i>m</i>	<i>g</i>	<i>u</i>	<i>y</i>	<i>e</i>	<i>n</i>	<i>i</i>
3	Torry		1	2		4	5		3			
4	Torry		1	3	2	4	4		4			
8	Dana		1	2		5	6	3	4			
29	Schrauf		1	3	2	6	7	5		4		8
31	Schrauf		1	6	2	3	4	4			7	
54	Des Cloizeaux		1	3	2		5	4				
55	Des Cloizeaux		1	2		4		3				

TABLE 5  
Middleton, Connecticut

Fig. no. in Gdt.	Observer	Form	010	100	001	130	111	201	160	131	110	211	011	221
			<i>b</i>	<i>a</i>	<i>c</i>	<i>m</i>	<i>u</i>	<i>e</i>	<i>y</i>	<i>o</i>	<i>g</i>	<i>n</i>	<i>k</i>	<i>s</i>
7	Johnston		2	3		6	4	5	1		7	7		
10	Dana		1	4	3	2	6	10	7	9	8	11	5	
18	Rose		1	3	2	8	5	4	9	6	10	7		
32	Schrauf		1	3	5	2	6	9		7	8	10	4	

TABLE 6  
Anneröd, Norway

Fig. no. in Gdt.	Observer	Form	010	100	201	111	211	001	110	130	085	131	150	121	101	221
			<i>b</i>	<i>a</i>	<i>e</i>	<i>u</i>	<i>n</i>	<i>c</i>	<i>g</i>	<i>m</i>	$\mu$	<i>o</i>	<i>z</i>	$\beta$	<i>i</i>	<i>s</i>
57	Brögger		1	3	2	7	5	4	6	8			9			
58	Brögger		1	2	3	5	4	6	8	7						
59	Brögger		1	2	10	5	3	6	9	4	7	8		11	12	13
60	Brögger		1	5	3	2	8	9	4	7	6					



TABLE 7  
Norway (Miscellaneous)

Fig. no. in Gdt.	Form Observer	010	100	111	201	130	001	110	150	101	211
		<i>b</i>	<i>a</i>	<i>u</i>	<i>e</i>	<i>m</i>	<i>c</i>	<i>g</i>	<i>z</i>	<i>i</i>	<i>n</i>
76	Milch	1		3	2	5		4			
78	Brögger	1	2	5	4	6	3	7			
79	Brögger	1	3	4	6	5	2	8	9		7
80	Brögger	1	3	4	6	2		5			
83	Brögger	1	4	3	2	5		6	7		
86	Brögger	1		2	4	5		3			
87	Brögger	1	2	5	4		6			3	

TABLE 8  
Black Hills, South Dakota

Fig. no. in Gdt.	Form Observer	010	130	100	170	011	131	150	201	133	111	032	211
		<i>b</i>	<i>m</i>	<i>a</i>	<i>d</i>	<i>k</i>	<i>o</i>	<i>z</i>	<i>e</i>	$\alpha$	<i>u</i>	<i>f</i>	<i>n</i>
67	Blake	1	2	4	3	5	5			7			
68	Blake	1	2	5	3	5	5	3		8		9	10
69	Blake	1	4	2		3	8		5		6		7

TABLE 9  
Standish, Maine

Fig. no. in Gdt.	Form Observer	010	001	100	130	110	111	011	131	201	150	121	211
		<i>b</i>	<i>c</i>	<i>a</i>	<i>m</i>	<i>g</i>	<i>u</i>	<i>k</i>	<i>o</i>	<i>e</i>	<i>z</i>	$\beta$	<i>n</i>
63	Dana	2	1	3	4	5	7	9	8	12	6	10	11
70	Dana	1	2	2	4	5	6			7			
71	Dana	1	2	3	4	7	8	4	6	9			

TABLE 10  
Rumford, Maine

Fig. no. in Gdt.	Form Observer	032	010	011	130	100	110	201	170	111	231	131	211
		<i>f</i>	<i>b</i>	<i>k</i>	<i>m</i>	<i>a</i>	<i>g</i>	<i>e</i>	<i>d</i>	<i>u</i>	$\pi$	<i>o</i>	<i>n</i>
72	Foote	2	1		4	3	5					6	
73	Foote	1	3	2	4		6	5	7	8	9	11	10

TABLE 11  
Paris, Maine

Fig. no. in Gdt.	Form Observer	170	001	100	010	110	130	131	211
		<i>d</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>g</i>	<i>m</i>	<i>o</i>	<i>n</i>
74	Warren	1	2	4	3	5	6	7	
75	Warren	1	2	3				5	4

TABLE 12  
Rabenstein Nr. Zwiesel, Bavaria

Fig. no. in Gdt.	Form Observer	010	001	100	130	201	160	111
		<i>b</i>	<i>c</i>	<i>a</i>	<i>m</i>	<i>e</i>	<i>y</i>	<i>u</i>
1	Leonhard	1	2	2	6	5	4	7
19	Rose	1	2	3	4	5		

The forms in the column headings are arranged from left to right in estimated order of decreasing importance for the locality considered. The number assigned to a form indicates its rank in the sequence of decreasing importance. This sequence for all the localities is in turn averaged and is presented in Table 13, in which the estimated sequence of decreasing importance for the species as a whole is shown in the column headings.

TABLE 13

Relative importance of forms according to localities

Table no.	Locality	Form	b	a	c	u	m	s	e	k	n	β	o	z	s	y	h	l	i	π	d	f	α	x	l	r	μ	σ	φ	R
			100	100	001	111	130	110	201	011	211	121	131	150	221	160	021	012	101	231	170	032	133	161	241	991	085	163	411	141
1	Greenland		1	7	8	2	5	4	16	3	12	13	13	24	10	21	6	9	19	11										
2	Bodennais		1	3	2	5	4	7	5	11	9	8	9	7	11		8	13	10											
3	Ilmen Mts.		1	2	10	3	5	6	4																					
4	Haddam		1	2	3	6	4	5	8	9																				
5	Middleton		1	2	3	5	4	9	6	11	10	8	12	7																
6	Anneröd		1	2	6	4	8	7	3	5	12	10	11	14																
7	Norway		1	2	6	3	5	7	3																					
8	Black Hills		1	3	10	2	8	5	12	6	7																			
9	Standish		1	3	2	6	4	5	9	7	12	11	8	10																
10	Rumford		2	5	9	4	6	7	3	12	11																			
11	Paris		4	3	2	6	5		8																					
12	Rabenstein		1	3	2	7	4	5																						

Fig. no.  
in Gdt.

Fig. no. in Gdt.	Observer	Phillips	Shepard	Mohs Zippe	Schrauf	Schrauf	Maskelyne	Strüver	Arzruni	Wada	Eakle	Lacroix
2	?	1	2	2	4	8	5	5				
6	Chesterfield, Massachusetts	1	2	3	4	5	5					
15	?	1										
44	?	1	8	2	2	7						
45	?	1	3	7	2	10	8					
51	Montevideo	1	3	2	6	5	8					
61	Craveggia, Ossola	1	2	4	3	8	6					
62	Sawarka, Urals	1	2	4	6							
77	Yamano, Japan	1	2	4	5	3	6	7				
88	Ramona, California	1	4		3	5	2					
90	Ankaratra, Madagascar	1			5	2	3	3				

N.B.—The localities from which only one crystal is figured in the *Atlas* are included in Table 13. The final sequence, obtained for the species as a whole, is shown in the column headings. Note that (*m, c*) *e k n* (*β, o*) *s y h i t π d f* (*α, x*) *l r μ σ φ R*

## DISCUSSION OF ZONAL CHARACTERS

The relative importance of the forms in each zone is determined from the above tables:

## A. "Central" zones.

(1) In the zone of the  $(hkk)$  faces, the observed order is:  $u \propto n \propto \phi$ . The face  $u$  is undoubtedly dominant in this zone, occurring always before  $n$  for every drawing in the *Atlas*, and found in twenty-three localities compared with seventeen for  $n$ .

(2) In the zone of the  $(lkl)$  faces, the order is:  $u (o \beta) x R$ . The face  $u$  is dominant, occurring twenty-six times, whereas  $o$  occurs only fourteen and is considerably smaller, in the observed figures. It is difficult to judge between  $o$  and  $\beta$ ; they are very nearly equal, with  $o$  perhaps a trifle larger. They are assigned equal importance.

(3) In the zone of the  $(hhl)$  faces, there are only two faces,  $u$  and  $s$ , shown on the projection (Fig. 1);  $r(991)$  is insignificant and has been omitted throughout in the calculations. The face  $u$  clearly dominates  $s$ , the occurrence ratio being 26:7.

These three central zones have a common dominant  $u$  which is therefore the unit face (111), confirming Goldschmidt's choice. The zone of the  $(hkk)$  faces is simple; the anomalies in the section considered are (311) and (122), both missing although  $\alpha(133)$ ,  $n(211)$  and  $\phi(411)$  are present. The zone of the  $(lkl)$  faces is also simple, in spite of the absence of (151) and the anomalously equal importance of  $o(131)$  and  $\beta(121)$ ; the faces present are  $u(111)$ ,  $\beta(121)$ ,  $o(131)$ ,  $R(141)$  and  $x(161)$ . Likewise the zone of the  $(hhl)$  faces is simple; (112) and (113) are missing but this anomaly does not obscure the character of the zone. If this conclusion were not evident at sight, it would follow of necessity from the two previous considerations, namely, the zones of the  $(hkk)$  and  $(lkl)$  faces are simple. Indeed if two central zones are simple, the third must be also, as it results from the theory of space groups.

## B. "Axial" zones.

(1) In the zone of the  $(0kl)$  faces the observed order of importance is:  $k(011)$ ,  $h(021)$ ,  $l(012)$ ,  $f(032)$ . This order holds for nearly every crystal drawing examined. Although these forms are rarely observed and are in no case observed together on the same crystal, yet where only one form occurs it is practically always  $k$ , which must therefore be the dominant. The forms  $h$  and  $l$  are about equal as regards frequency of occurrence; neither is definitely larger than the other. This is the zone which does not conform to the space-group found by  $x$ -ray work: it therefore deserves



closer analysis. There are five localities where  $(0kl)$  faces have never been observed, *viz*: the Ilmen Mts.; Haddam, Conn.; Norway; Paris, Me., and Rabenstein. Of the remaining localities Greenland gives the most complete data. On the sixteen crystals figured,  $k$  occurs in every case,  $h$  and  $l$  occur jointly on eight crystals with varying relative importance;  $h$  is found alone on four crystals and  $l$  also alone on four crystals. With two exceptions these observations indicate that  $k$  is the dominant, the other two indicate  $h$  as the most important face. The order may safely be written  $k(h, l) f$ . Data on the localities, not previously mentioned, are as follows: at Bodenmais, from eleven figures, Lévy reports  $k$  once and Schrauf reports  $l$  once:  $k$  is more important than  $l$ . At Middleton, Conn.,  $k$  alone is observed on two of the four figures. Three crystals from the Black Hills all show  $k$ , and  $f$  is observed on one; here  $k$  is more important than  $f$ . Three crystals from Standish, Me., and two from Rumford, Me., show  $k$  twice and  $f$  once, respectively. For other localities, each represented by one figure,  $k$  occurs four times;  $h$ , four times;  $l$ , three times. In none of the crystals drawn is  $l$  the dominant of the zone. It is regrettable that there is not more information regarding these forms. However, from the available morphological data, we must conclude that this is a simple zone with  $k(011)$  dominant.

(2) In the zone of the  $(h0l)$  faces there are only two forms:  $e(201)$  and  $i(101)$ , of which  $e$  is undoubtedly the dominant, as it occurs forty-three times whereas  $i$  occurs only nine. This is a simple zone with the dominant "shifted" from unit position toward  $a$ .

(3) In the zone of the  $(hk0)$  faces the following forms occur:  $g(110)$ ,  $m(130)$ ,  $z(150)$ ,  $y(160)$ , and  $d(170)$ . The forms  $g$  and  $m$  show equal observed importance in the final order; it is impossible to give more weight to one than to the other. However, despite this and the anomaly of  $y$  being more important than  $d$ , the zone can only be interpreted as double with  $g$  dominant.

### C. Pinacoids.

In relative importance the three pinacoids rank as follows:  $b$ ,  $a$ ,  $c$ . With very few exceptions,  $b$  is the largest face on the figures studied and in most cases  $a$  is observed to be more important than  $c$ .

## SPACE-GROUP DETERMINATION FROM MORPHOLOGICAL DATA

A gnomonic projection (Fig. 1) is drawn to present the observed data. All forms are plotted except  $\sigma$   $r$   $\mu$   $\alpha$  which either are doubtful or have such high indices that they cannot be considered in the discussion of zonal character. The approximate importance of the various forms is

shown by the size of the gnomonic poles. For the less important forms this method of notation is of necessity less accurate. The scale of poles on the left hand side of the projection represents the zone of the  $(hk0)$  faces and is a gnomonic projection on the side pinacoid  $b$ . Another projection, on the front pinacoid  $a$ , is shown at the bottom of the figure.

The conclusions derived from the above study are summarized in a stereographic projection (shown in the lower right hand corner, Fig. 1). In this inset the zonal character is interpreted in each case; a double line representing a double zone and a single line representing a simple zone. Faces with coprime indices are represented by black dots; faces with doubled indices, by open circles. The dominant face only is shown in each zone.

If we examine the results in the previous section, we see that the three central zones are simple and have a common dominant  $u(111)$ . Therefore the lattice is a primitive lattice ( $P$ ), with  $(111)$  dominant. This is in agreement with Goldschmidt's setting. Next we consider the axial zones. The zone of the  $(0kl)$  faces is a simple zone with the unit face  $k(011)$  dominant, hence the  $(100)$  plane, if a plane of symmetry, is not a glide plane. The zone of the  $(h0l)$  faces is a simple zone with  $e(201)$  dominant, i.e. the dominant is "shifted" toward  $a$  and consequently the  $(010)$  plane is an  $a$  glide plane of symmetry. The zone of the  $(hk0)$  faces is a double zone with the unit face  $g(110)$  dominant, hence the  $(001)$  plane is an  $n$  glide plane of symmetry (Donnay, 1938). From these considerations the symbol of the *morphological aspect* (Donnay-Harker, 1937) is  $P^*an$ . It also follows that the pinacoids must be written  $c\{001\}$ ,  $a\{200\}$ ,  $b\{020\}$ , in terms of the *multiple indices* (Donnay-Harker, 1937).  $P^*an$  corresponds to two space-groups:  $Pman$  in the holohedry  $(2/m\ 2/m\ 2/m)$ , and  $P2an$  in the antihemihedry  $(2\ m\ m)$ . The symmetry class  $2\ m\ m$  is ruled out because, in the present setting, the  $z[001]$  axis is an axis of two-fold symmetry.

If we consider the multiple indices of the pinacoids  $a\{200\}$ ,  $b\{020\}$ ,  $c\{001\}$ ; the effective interplanar spacings will be in the ratios  $d_{200}:d_{020}:d_{001}=0.2012:0.5:0.3580$ . Thus the theoretical order of importance of these forms would be  $b\ c\ a$ , as against the observed rank  $b\ a\ c$ . This is an anomaly to the generalized law of Bravais.

Despite the anomalies encountered in our interpretation of the zonal characters and the relative importance of the pinacoids, it is plain that the morphological data lead to a unique determination of the space-group  $Pman$ .

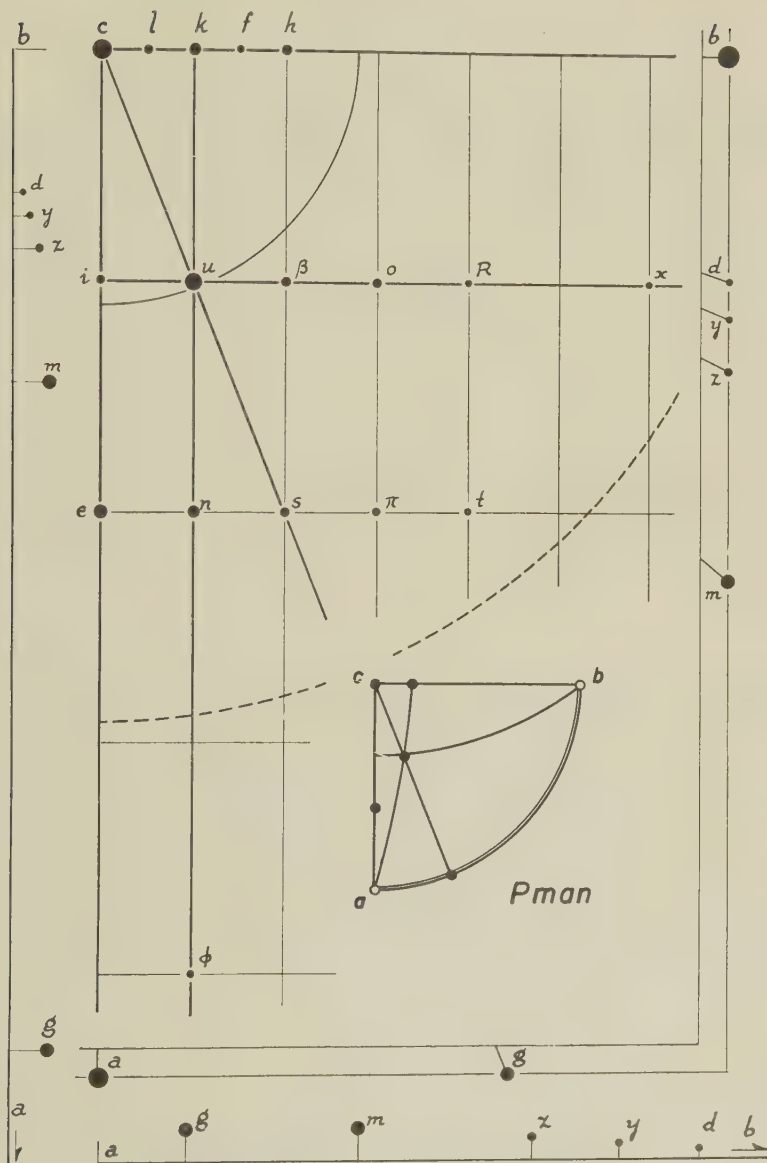


FIG. 1

Gnomonic projection of columbite:

$$a:b:c=0.4023:1:0.3580 \quad p_0:q_0:r_0=0.8899:0.3580:1$$

The radius of the solid arc is that of the sphere of projection ( $r_0=1$ ). The radius of the dotted arc is that of the sphere of Bravais probability. The inset shows a stereographic projection of the main zones and derivation of the space group.

### COMPARISON BETWEEN THE CLASSICAL LAW OF BRAVAIS AND THE GENERALIZED LAW

The theoretical order of decreasing importance of the forms in columbite crystals is determined, for the two laws, by a graphical method (Peacock, 1938). A *sphere of Bravais probability* (Peacock, 1938) is taken with a radius large enough to include most of the important forms and small enough to avoid consideration of too many unknown forms. It is indicated by the dotted arc on the projection, Fig. 1. In Table 14, the two laws are compared; the first column, headed  $P^{***}$ , and the second column, headed  $P_{man}$ , show the forms, in decreasing order of importance, according to the classical law and the generalized law, respectively. In the last three columns a direct comparison is made; the first column shows the forms peculiar to the classical law, the center column has the forms common to both laws, and the last column, the forms which only occur with the generalized law. It will be seen that there are many more anomalies in the classical law than in the generalized law. Therefore, from the point of view of the forms observed, the second law, although not perfect, is more satisfactory.

### COMPARISON WITH X-RAY RESULTS

J. H. Sturdivant (1930), using the oscillation and the Laue methods, has found a set of x-ray extinctions leading to a space-group, which in our setting is  $P_{can}$ . It will be seen that the morphological development of the space-group is confirmed insofar as it concerns all the central zones of  $(hkl)$  faces and the axial zone of  $(h0l)$  and  $(hk0)$  faces. However, the morphology of the zone of the  $(0kl)$  faces indicates that the  $(100)$  plane is a mirror plane of symmetry whereas Sturdivant's results show it to be a  $c$  glide plane. As for the pinacoids, the Sturdivant space-group demands the halving of all three, hence they must be written  $a\{200\}$ ,  $b\{020\}$ ,  $c\{002\}$ , which leads to the theoretical order  $b\ a\ c$ , identical with that of the classical law of Bravais and in agreement with the observed fact.

Professor Martin A. Peacock has kindly checked and confirmed the Sturdivant space-group by means of Weissenberg pictures taken on Topsham, Me., material. The case of columbite, therefore, appears to be one of bona fide conflict between the x-ray results and the morphological data for the zone of the  $(0kl)$  faces. Does the structural arrangement of atoms in columbite simulate a mirror plane of symmetry where the  $c$  glide plane actually exists? Is it similar, in this respect, to NaCl, which, although face-centered, acts like a primitive cubic lattice in the morphological development? These questions cannot be answered positively with the available structural data.



TABLE 14. COMPARISON OF THE CLASSICAL LAW OF BRAVAIS ( $P^{***}$ )  
WITH THE GENERALIZED LAW ( $P_{man}$ )

Theoretical sequences of forms in order of decreasing importance

$P^{***}$	$P_{man}$	Comparison		
		$P^{***}$	Common	$P_{man}$
$b$ 010	$b$ 020	$b$ 010	—	
$a$ 100	$g$ 110		—	$b$ 020
$g$ 110	$c$ 001	$a$ 100	—	
$c$ 001	$k$ 011		$g$ 110	
$k$ 011	$h$ 021		$c$ 001	
120	$u$ 111		$k$ 011	
$h$ 021	$m$ 130	120	—	
$i$ 101	031		$h$ 021	
$u$ 111	$\beta$ 121	$i$ 101	—	
$m$ 130	$o$ 131		$u$ 111	
031	041		$m$ 130	
$\beta$ 121	$a$ 200		031	
140	$R$ 141		$\beta$ 121	
$o$ 131	$z$ 150	140	—	
041	$l$ 012		$o$ 131	
210	$e$ 201		041	
$R$ 141	051		—	$a$ 200
$z$ 150	$n$ 211	210	—	
$l$ 012	$s$ 221		$R$ 141	
$e$ 201	151		$z$ 150	
051	240		$l$ 012	
$n$ 211	$f$ 032		$e$ 201	
230	$\pi$ 231		051	
$s$ 221	061		$n$ 211	
151	$t$ 241	230	—	
$f$ 032	$x$ 161		$s$ 221	
$\pi$ 231	$i$ 202		151	
$y$ 160			$f$ 032	240
061			$\pi$ 231	
$t$ 241		$y$ 160	—	
$x$ 161			061	
			$t$ 241	
			$x$ 161	
			—	$i$ 202

N.B.—Known forms are indicated by the Goldschmidt letters.

## TRANSFORMATIONS

In the Schrauf, 1877 V. Goldschmidt, 1913- Taylor, 1939 setting, the structural unit cell has the following identity periods (Sturdivant's values):

$$a_0 = 5.730 \text{ \AA}, b_0 = 14.238 \text{ \AA}, c_0 = 5.082 \text{ \AA}.$$

The various cells used by other authors, and their respective settings, are shown in Fig. 2 and explained in Table 15.

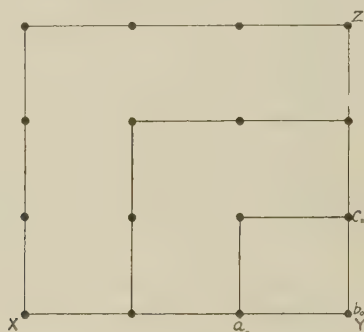


FIG. 2. The lattice of columbite.

TABLE 15

Transformation of settings

	Dana 1892	V. Gold- Schmidt 1886	Schrauf, 1877 V. Gold- schmidt, 1913 Taylor, 1939	Groth { 1882 1889	Breithaupt, 1858 Sturdivant, 1930	Schrauf 1864
<i>X</i>	$3a_0 = \bar{b}$	$a_0 = b$	$a_0 = a$	$2a_0 = a$	$a_0 = \bar{c}$	$a_0 = \bar{b}$
<i>Y</i>	$b_0 = \bar{a}$	$b_0 = c$	$b_0 = b$	$b_0 = b$	$b_0 = \bar{b}$	$b_0 = \bar{a}$
<i>Z</i>	$3c_0 = \bar{c}$	$c_0 = a$	$c_0 = c$	$2c_0 = c$	$c_0 = \bar{a}$	$c_0 = c$

N.B.—In each column, *a*, *b*, *c*, indicate the *a*, *b*, *c*, of the author considered.

It is seen that only three cells have been used; all of which have the same length in the direction of Taylor's *b*-axis. In the directions of Taylor's *a* and *c*, the lengths are in some cases the same and in other instances doubled or tripled. The other differences lie in the setting adopted. Among those who have correctly chosen the unit cell, the settings used are as follows:

V. Goldschmidt, 1886	$a < b < c$
Schrauf, 1877	$c < a < b$
V. Goldschmidt, 1913	
Taylor, 1939	
Breithaupt, 1858	$a < c < b$
Sturdivant, 1930	
Schrauf, 1864	$c < b < a$

The convention  $c < a < b$  is chosen for this paper in accordance with recent proposals (Donnay and Mélon, 1933; Donnay, Tunell and Barth, 1934; Peacock, 1937).

Table 16 summarizes the transformations with correct fractional values.

TABLE 16  
Transformation Matrices

From To	Dana, 1892	V. Goldschmidt, 1886	Schrauf, 1877 V. Goldschmidt, 1913 Taylor, 1939	Groth, (1882 (1889	Breithaupt, 1858 Sturdivant, 1930	Schrauf, 1864
Dana, 1892	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{1}{2} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{1}{2} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \frac{1}{2} \\ 1 & 0 & 0 \\ 0 & \frac{1}{2} & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$
V. Goldschmidt, 1886	$\begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & \bar{3} & 0 \\ \bar{3} & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 2 & 0 \\ 0 & 0 & 1 \\ 2 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}$
Schrauf, 1877 V. Goldschmidt, 1913 Taylor, 1939	$\begin{pmatrix} 0 & \bar{1} & 0 \\ \bar{3} & 0 & 0 \\ 0 & 0 & \bar{3} \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$
Groth, (1882 (1889	$\begin{pmatrix} 0 & \bar{1} & 0 \\ \frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \frac{1}{2} \\ \frac{1}{2} & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \frac{1}{2} \\ 0 & \bar{1} & 0 \\ \frac{1}{2} & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} & 0 \\ \frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$
Breithaupt, 1858 Sturdivant, 1930	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 3 \\ 3 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \bar{2} \\ 0 & \bar{1} & 0 \\ \bar{2} & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$
Schrauf, 1864	$\begin{pmatrix} \frac{1}{2} & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & \bar{1} \\ 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & \bar{1} & 0 \\ \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}$	$\begin{pmatrix} 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

Dana (1892) = Rose (1845), Hausmann (1847), Miller (1852), Des Cloizeaux (1855).

## ACKNOWLEDGMENTS

I wish to thank Professor J. D. H. Donnay for his assistance and advice during the preparation of this paper both at the Johns Hopkins University and at the Université Laval. It is also a pleasure to record my indebtedness to Professor M. A. Peacock, of the University of Toronto, who kindly re-determined the space-group of columbite by Weissenberg photographs, as our own equipment was not available at the time. My thanks are also due to Mr. Martin L. Ehrmann, of New York City, and to Dr. W. E. Richmond, of Harvard University, who courteously provided suitable columbite crystals.

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## OCCURRENCE OF FELDSPAR REPLACING FOSSILS

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A study of some rock specimens from Provo River damsite No. 8 in Provo Canyon, Utah, brings to light an unusual occurrence of feldspar crystals in limestone, which in many instances are contained within skeletons of fossils. The obvious non-clastic derivation of the feldspar, together with the abundant evidence supporting authigenesis, suggests that the feldspar may be of this origin. The writer desires to extend his thanks and appreciation to Professors Paul F. Kerr and Phillip Krieger, and Dr. H. N. Coryell of the Columbia University faculty for their encouragement and advice during the preparation of this paper.

The sedimentary series in which the beds containing the feldspar is located, was mapped by the 40th Parallel Survey as Carboniferous.<sup>1</sup> The areal position of the bed indicates that it is within the Brazer formation of upper Mississippian age, but the identification of two genera of Bryozoa, *Strombopora* and *Rhombopora*, by Dr. H. N. Coryell, however, signifies that it might better be placed within the Pennsylvanian.

The bed containing the feldspar is approximately 7 ft. thick. Its strike is nearly due north-south and it dips 60° to the east. The exposure is in the bottom of the Provo gorge, about one quarter of a mile north of the Utah-Wasatch County line. At this point the Provo River flows south-eastward and cuts obliquely across the strike just north of the exposure. Therefore the stream gravels cover the outcrop of the bed to the north, while to the south a thick mantle obscures the outcrop. Thus extensive observation of the bed along its trace is prevented in either direction.

The rock containing the feldspar is a dense black limestone with a few irregular fractures filled with calcite. Bedding laminae are essentially absent. A few megascopic brachiopods were present but an accurate identification of them could not be made. An occasional crinoid stem could also be seen with the unaided eye. On a polished surface of the rock many other small fossils were observed, but it was necessary to resort to the microscope to more definitely determine their character. Microscopically, the limestone consists of a matrix of fine grained carbonate with occasional coarsely crystalline calcite veinlets. Many fossils and fragments of fossils are imbedded in the matrix. The recognizable forms are brachiopods, crinoid arms and stems, pelecypods and bryozoa. Throughout are present many small quartz grains with sub-rounded outlines constituting about 2 per cent of the rock. They have a random distribution and are usually confined to the carbonate matrix between the fossils, and appear to be of clastic origin. Quartz also occurs as a fos-

<sup>1</sup> King Surveys, *Atlas Sheet No. 50, U. S. Geol. Survey*, West of 100th Meridian.

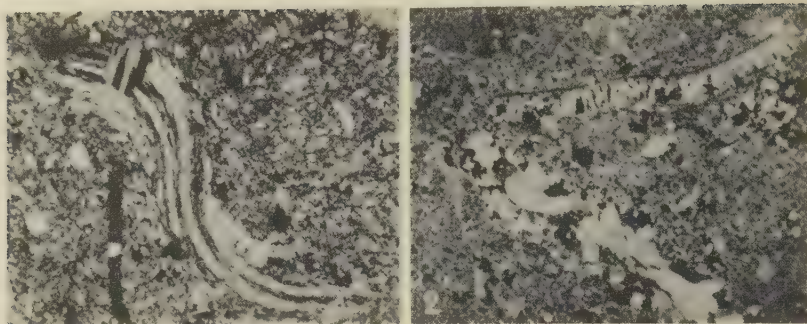


FIG. 1. Photomicrograph ( $\times 60$ ) with crossed nicols. Shows a fossil fragment composed of fine carbonate which has been replaced by a well shaped feldspar crystal. Observe many irregularly shaped quartz grains of varying sizes distributed in the dense carbonate matrix. Quartz also appears replacing the fossils.

FIG. 2. Photomicrograph ( $\times 17$ ) with crossed nicols. This shows part of a large elongate fossil (lower left center) almost completely replaced by quartz and feldspar. Immediately adjacent (upper center) is a fossil composed of carbonate which has been unaffected by replacement except for two minute quartz crystals (upper right).

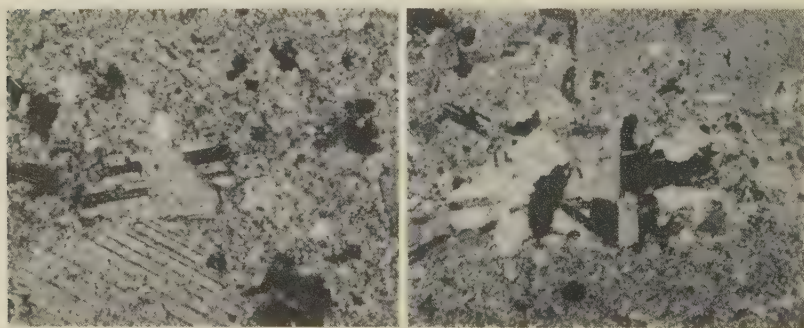


FIG. 3. Photomicrograph ( $\times 100$ ) with crossed nicols. A large well formed feldspar crystal 0.23 mm. long has grown almost entirely in the matrix, only slightly replacing the crinoid arm (lower right center). Smaller crystals of feldspar and quartz can be seen throughout the illustration. Note the dolomite crystal which has developed within the large feldspar.

FIG. 4. Photomicrograph ( $\times 53$ ) with crossed nicols. This feldspar crystal is 0.3 mm. in its greatest dimension and has replaced a fossil, whose outline in places has been obliterated by feldspar growth beyond its borders. The fossil extends from left to right across the center of the photomicrograph.

sil replacement. The anhedra are varied in size and generally have interlocking relations with one another.

Feldspar often accompanies the replacement of quartz, and apparently is contemporaneous in formation, and although predominantly anhedral in shape, there are a few instances where it is euhedral. Excellent albite twinning is present in all crystals. Figures 2 and 4 show fossils which have been replaced almost entirely by quartz and feldspar. In many cases (Fig. 2) the replacing material is confined within the fossil outlines. In an exceptional case (shown in Fig. 4) the feldspar has disregarded the outline of the fossil and has developed beyond it. Many fossils have been only partially replaced (Fig. 2).

The greatest amount of the feldspar is present in the fine carbonate matrix of the rock. In no case is quartz intimately associated with it here. The crystals are all exceptionally well formed, presenting good crystalline outlines, the largest of which is approximately 0.23 mm. in its greatest dimension (see Fig. 3). They range from this size down to minute submicroscopic crystals and are oriented at random and form no grouping whatsoever. Figure 1 shows a well formed crystal partly within and partly without the fossil. In many cases the feldspar and the quartz are replaced by dolomite, which is distinctly of later development (Fig. 3). The occasional carbonate veinlets which traverse the rock, cut feldspar and quartz alike, and are therefore considered to be of later development.

A fragment of the rock was dissolved in hydrochloric acid and the resulting residue was found to be about 20 per cent of the whole and consisted of black carbonaceous clay, quartz and feldspar. The solute was tested for sulphate and magnesium, which resulted negatively for sulphate, but considerable magnesium was found. With the aid of a binocular microscope, some excellent feldspar crystals were separated from the residue. These were found to be triclinic and elongated parallel to the *c*-axis. The forms (001) and (010) were well developed, while (110) and (101) were less frequent. Marked (001) cleavage was noted. The indices were determined as  $\alpha = 1.5320$ ,  $\beta = 1.5365$  and  $\gamma = 1.5414$ , which according to Rogers and Kerr<sup>2</sup> are the indices for a plagioclase of  $\text{Ab}_9\text{An}_1$  composition. The expected large  $2V$  was present, but could not be accurately measured because of the small size of the crystals. The crystals were clear and free of inclusions, but occasionally ragged edges were noted which are evidently due to the partial replacement by dolomite. Albite twinning was invariably present.

<sup>2</sup> Rogers and Kerr, *Thin-Section Mineralogy*, McGraw-Hill, 214 (1933).

## ORIGIN

An effort was made to discover a suitable hypothesis of origin which would account for the presence of these feldspar crystals in this apparently unaltered fossiliferous limestone. Hydrothermal introduction, or other high temperature source, was considered with rather discouraging results. So far as known, there is no igneous rock exposed within at least 15 miles of the point where the specimens were taken. The nearest known metaliferous mineralization is at least 10 miles away. A source for high temperatures other than burial would seem to be essentially lacking. The veinlets in the rock, which were evidently made during folding, contain carbonate only and appear to have been formed after the time of formation of the feldspar, and are therefore entirely unrelated to it. It is on this evidence that metamorphism during folding has not been seriously considered. The lack of veinlets, grouping or segregation of crystals of feldspar indicated that their position has not been controlled by secondary structures within the limestone. Minerals resulting from hydrothermal action on impure limestone are entirely absent, also the clastic quartz grains or feldspar crystals were not observed to be enlarged by secondary growth.

The rock in general presents an unaltered appearance with even the original carbon content relatively unaffected. Calcite is one of the more easily recrystallized minerals, but the character of the original carbonate of the rock remains unchanged even to the fine delicate structures of the unreplaced fossils (Fig. 2). The only direct evidence suggesting that introduction has taken place is the incongruity of non-clastic feldspar in a sedimentary rock, but since such an association has been observed before and an origin of authigenesis given, it seems reasonable and proper that this origin should be seriously considered for this occurrence.

A. Drian<sup>3</sup> in 1861 first described an occurrence of feldspars in dolomite of the Alpine Trias and suggested that sedimentary processes were responsible for their formation. Since then many occurrences of authigenic feldspars have been observed. It has been generally accepted that feldspars can, and do, form by this process, but the exact definition and description has varied somewhat with different authors. Several workers hold the view that feldspars form during deposition of the sediment or shortly after. Grandjean<sup>4</sup> went so far as to state that feldspars, thus

<sup>3</sup> Drian, A., Notice sur les cristaux d'albite renfermés dans les calcaires magnésiens des environs de Modane: *Bull. soc. géol. France*, ser. 2, **18**, 804-805 (1861).

Note. The information from the French publications cited was obtained from abstracts in *Mineralogy of Sedimentary Rocks* by P. G. H. Boswell. Thomas Murby & Co. 1933.

<sup>4</sup> Grandjean, F., Deuxième note sur le feldspath néogène des terrains sédimentaires non métamorphiques: *Bull. soc. franc. min.*, **33**, 92-97 (1910).



forming, cease to grow on the sea floor after burial. J. de Lapperent<sup>5</sup> suggests that organic action was the "first cause" of the formation of this type of feldspar. Singewald and Melton<sup>6</sup> believe that a moderately high temperature, attained after burial, is the responsible factor. Reynolds<sup>7</sup> suggests that they may grow long after deposition and perhaps after consolidation through introduction of the alkalis by ground water and their absorption by clay material. Tester and Atwater<sup>8</sup> found feldspars being formed after dolomitization of limestones had begun.

Most of the authigenic feldspar found by these authors contained carbonaceous or other inclusions. Daly,<sup>9</sup> however, describes glass-clear feldspar and gives them an authigenic origin.

If it were not for the fact that the feldspar here described replaces fossils, and is present only as disseminated crystals in the lime matrix, little objection would be found in accounting for it through the process of authigenesis. The question arises then: can authigenic feldspars replace fossils during growth? An authigenically growing crystal in a lithified or partly lithified rock must replace the material in which it is imbedded. Therefore it does not appear unreasonable to assume that they could replace a fossil. All the constituents necessary to make up the feldspar are present within the rock. The alumina and silica are present as clay material and quartz grains. The calcium is abundantly present in the calcite. The soda may have been present in the connate water of the rock or it may have been introduced by ground water, as suggested by Reynolds.<sup>10</sup> Proof of either origin of the soda is lacking.

As to the exact temperature at which the feldspar formed, the writer is unable to state, but it certainly must have been moderate. Daly<sup>11</sup> states that feldspars have been made synthetically as low as 300°C., by K. Chrustschoff, using a considerable amount of time in the process. Daly also states that according to Doelter, feldspars can form at 100°C. and he further suggests that they may form as low as 70°C.

In the writer's opinion such an origin best explains the presence of the

<sup>5</sup> de Lapperent, J., Sur les cristaux de feldspaths développés dans les calcaires du Crétacé supérieur pyrénéen: *Compt. rend. acad. sci. Paris*, **167**, 784-786 (1918).

<sup>6</sup> Singewald, J. T., and Melton, C., Authigenic feldspar in limestone at Glen Falls, New York: *Bull. Geol. Soc. Am.*, **40**, 463-468 (1929).

<sup>7</sup> Reynolds, D. L., Some new occurrences of authigenic feldspar: *Geol. Mag.*, 390-399 (1929).

<sup>8</sup> Tester, A. C., and Atwater, G. I., The occurrence of authigenic feldspar in sediments: *Jour. Sed. Petrology*, **4**, 23-32 (1934).

<sup>9</sup> Daly, R. A., Low temperature formation of alkaline feldspars in limestone: *Proc. Nat. Acad. Sci.*, **3**, 659-665 (1917).

<sup>10</sup> Reynolds, D. L., *Op. cit.*

<sup>11</sup> Daly, R. A., *Op. cit.*

feldspar in this limestone. It was obviously formed after deposition of the limestone and likely after consolidation, but before the folding, thereby eliminating a metamorphic consideration. The necessary chemical constituents were present in the original rock as a result of sedimentation with perhaps a little introduction of soda by ground water. The temperature was very low, perhaps near that of ground water. During growth some of the fossils were replaced by quartz as well as feldspar. Perhaps a more fitting explanation for the presence of the feldspar in this limestone, other than hydrothermal or authigenic origin, can be found. Up to the present time, however, no other satisfactory solution has presented itself.

## NOTES AND NEWS

### DETRITAL DIHEXAHEDRAL CRYSTALS OF QUARTZ IN A SEDIMENT IN UPPER MAGDALENA VALLEY OF COLOMBIA, SOUTH AMERICA\*

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#### INTRODUCTION

Dihexahedral crystals of quartz were observed as a relatively abundant detrital component in a wide-spread sedimentary formation which occurs in the Upper Magdalena Valley of Colombia, South America. The occurrence merits attention because of its unusual character, the relative abundance of well developed crystals, the diagnostic possibilities of the quartzoids in making stratigraphic correlations, and the bearing of the mineral on the volcanic history of the Central Cordillera of the Colombian Andes.

#### LOCATION AND DISTRIBUTION

The dihexahedral crystals of quartz were first observed in a coarse, conglomeritic, loosely consolidated sandstone on the western margin of the Upper Magdalena Valley some 23 kilometers, by road, south of Ibagué, Tolima, where the Coello River emerges from the rugged topography of the Cordillera Central and flows eastward in a deep canyon incised in the llanos, or plains, of Tolima (Fig. 1). The quartzoid-bearing conglomeritic sandstone caps the llanos in this area.

The crystals were observed also as a component of the "Guamo sand," which is used extensively as a construction material, and which occurs some 55 kilometers southeast of Ibagué, in the vicinity of Guamo.

Likewise, the quartzoids occur in similar sands that form depositional terraces upstream along the Coello River, within the gorge that passes through the crystallines of the Cordillera Central. Further, spotty and patchy erosional remnants of the quartz-bearing sands were observed in the valley between Ibagué and Ambalema.

These widely scattered occurrences of sediments containing the quartzoids suggest that they have, or at least once did have, a fairly extensive distribution, the details of which remain to be determined by future studies. Field and laboratory observations upon which this article are based were made in May 1938 during the course of investigations for the Departamento de Petróleos, Ministerio de Industrias y Trabajo, of the Colombian Government.

\* Published by permission of the Jefe de la Comisión Científica y el Departamento de Petróleos, Bogotá, Colombia.

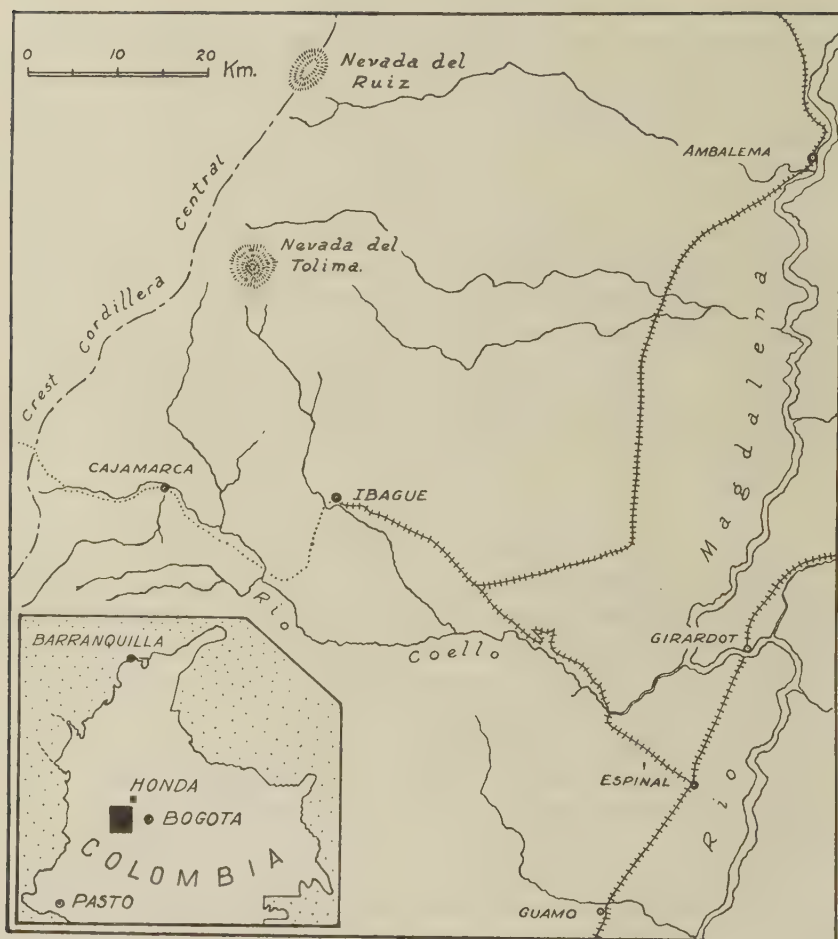


FIG. 1. Location map.

## DESCRIPTION

The quartz of the dihexahedral crystals found in the Magdalena Valley is a colorless, transparent variety (Fig. 2-A). The identity of the mineral was checked in the Laboratorio de Minas y Petróleos, Bogotá, and the mineral showed properties in agreement with published data on quartz. Many crystals have perfect dihexahedral forms,  $r$  ( $10\bar{1}1$ ) and  $z$  ( $01\bar{1}1$ ) being equally developed, but some distortion is common. Well formed quartzoids range in length between 0.5 mm. and 5.0 mm.



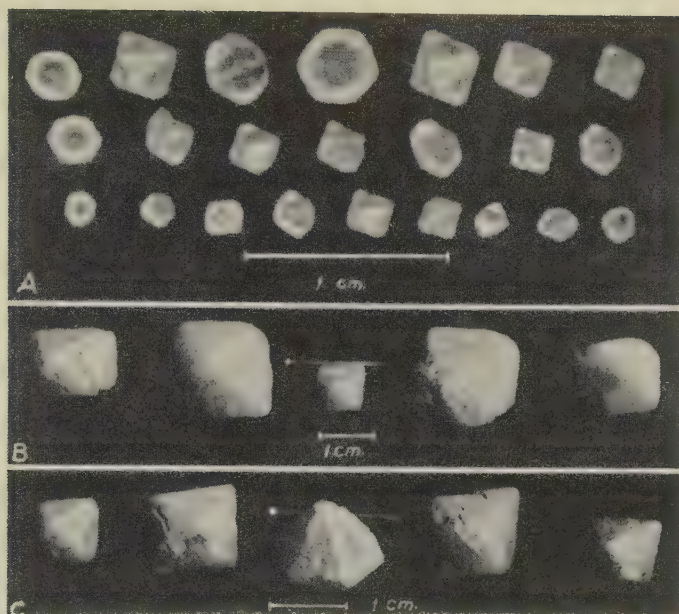


FIG. 2-A. Detrital dihexahedral crystals of quartz collected from the top of the Mesa formation near the Coello River.

FIG. 2-B, C. Larger dihexahedral crystals of quartz collected from along the Coello River in the Cordillera Central near Cajamarca. Most of the crystals illustrated are placed so that the  $c$ -axis slopes upward from left to right. Parallel grouping is well shown in many of the larger crystals.

Note how abrasion has rounded the apices of some of the larger crystals in Fig. 2-B. Short prism faces occur in the first and third crystals from the left in Fig. 2-C.

Many crystals have sharp edges to the crystal faces. Some crystals are broken, but only the largest ones show any tendency to be rounded as a result of transportation. When rounding is present it is best developed at, or restricted to, the apices of the pyramids. Some of the crystals have indentations and embayments characteristic of mutual penetration with neighboring minerals during growth in a magma.

Quartzoids larger than those found in the Magdalena Valley occur in terraces in the upper reaches of the Coello River far within the Cordillera Central. These range in size up to 2 cm. from apex to apex (Fig. 2-B, C). In some places near the town of Cajamarca (San Miguel), Tolima, they are plentiful enough to be sought out by the boys to shoot in their sling shots. These larger crystals are translucent and cloudy in contrast to the clear glassy character of the smaller ones described above. Much of the

cloudy appearance is due to internal flaws. The larger quartzoids are usually badly distorted and may be quite rounded at their apices due to abrasion during transportation. Indentations characteristic of corrosion or mutual penetration with other minerals are present in many specimens and parallel grouping is common. Short prism faces,  $m$  (10 $\bar{1}0$ ), are present on some crystals.

#### OCCURRENCE

Dihexahedral crystals of quartz are known throughout the literature to be of igneous origin and their expectable occurrence is in dacitic and

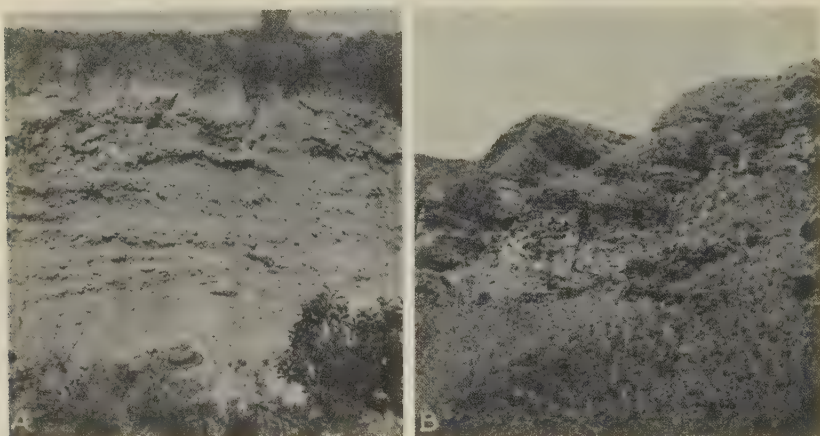


FIG. 3-A. A typical outcrop from which small dihexahedral crystals were collected.

FIG. 3-B. Typical bluff of the Mesa formation.

rhyolitic types of rocks. Although quartz-bearing sands are common, the occurrence of well formed quartzoids as a relatively abundant detrital component of a sediment is unusual and warrants attention; the writer is not aware of previous notice of such an occurrence.

The quartz crystals occur in a coarse, conglomeritic, loosely consolidated sandstone (Fig. 3-A) whose fragments consist chiefly of quartz, feldspar, ferromagnesian minerals, and andesitic and dacitic rock fragments. Pieces of pumaceous lavas, plutonic and metamorphic rocks are also present. The associated single mineral grains include feldspar, mostly of andesine variety, hornblende, pyroxene, biotite and magnetite; good euhedral forms are common, and the pyriboles occur in much smaller sizes than the lighter minerals. Bedding is well defined, especially on weathered slopes.

Where first observed, the quartzoid-bearing sandstone caps the "llanos deposit," or Mesa formation, which comprises ash, pyroclastics and mixed sediments, mostly water-worked, that aggregate a thickness of over 500 feet in this locality, but exceed 1,000 feet in thickness near Honda, Tolima. The Mesa formation (Fig. 3-B) is essentially an alluvial plain deposit built up by intersecting alluvial fans that were deposited from the Cordillera Central. The age of the formation has been variously stated as ranging from Pliocene to Recent. The formation was deposited after folding, faulting and erosion of an appreciable thickness of Miocene strata, for which reason the writer considers it to be latest Pliocene or earlier Pleistocene in age.

### ORIGIN

The dihexahedral quartz crystals obviously are of igneous origin, having been developed under intratelluric conditions, and quartzoid-bearing rocks have been described from the general region. Hettner and Linck<sup>1</sup> described boulders from the Honda district that were pyroxene-bearing amphibole andesite containing dihexahedral quartz crystals; the boulders were transported from the Cordillera Central.

Küch<sup>2</sup> described quartzoids in pyroxene-amphibole dacite from the Mesa Nevada de Hervo (Paramo de Ruiz), and from a boulder of agglomerate of biotite, amphibole-dacite which he collected from the Coello River near Ibague. He also described dacites in which dihexahedral crystals of quartz occur from localities south of the drainage basin of the Rio Coello, especially in the vicinity of Tuquerres near Pasto.

Lehmann<sup>3</sup> noted the occurrence of dihexahedral quartz crystals in a quartz-monzonite from west of Coyaima, Tolima.

The striking fact that many of the crystals are not appreciably rounded by abrasion suggests, with due allowance for the hardness of the mineral, that they have undergone little transportation by water. It seems likely that many of the crystals were brought to the earth's surface and scattered by a more or less explosive type of volcanism, during which they were shaken loose from the magma along with other already formed crystals. This means of liberation of minerals is known to have taken place in other volcanic regions. The presence of pumaceous

<sup>1</sup> Hettner, A., and Linck, G., *Beitrage zur Geologie und Petrographie der Columbianischen Anden*, p. 200 (1888).

<sup>2</sup> Küch, R., *Petrographie 1. Die vulkanischen Gesteine in Geologische Studien in der Republik Colombia*. Reiss, W., und Stübel, A., *Reisen in Sud-Amerika*. Berlin, verlag von A. Asher & Co. p. 91 (1892).

<sup>3</sup> Lehmann, E., *Beitrage zur Petrographie des Gebietes am obern Rio Magdalena: Tschermak's Min. und Pet. Mitteil.*, 260 (1911).

fragments of lava and free fragments of feldspars and pyriboles in the sediment support this hypothesis.

In addition, important quantities of the quartzoids were subsequently liberated from their parent rocks by the usual processes of weathering, disintegration and fluvial erosion.

#### STRATIGRAPHIC SIGNIFICANCE

To date the dihexahedral quartz has been observed in abundance only at the top of the Mesa formation. In places the Mesa formation appears quite similar lithologically to the tuffaceous facies at the upper part of the underlying Miocene Honda series. As far as the writer's brief observations go, the two formations, when lithologically similar, may be differentiated in places by the presence of abundant small quartzoids in the younger Mesa formation. One purpose of this article is to call attention to the stratigraphic significance of the presence of the crystals in the hope that future investigations may include detailed study of the distribution of the quartzoids throughout the stratigraphic section and check their value as a field criterion for differentiating between the Mesa formation and the Honda series in the upper Magdalena Valley.

The presence of quartzoids offers a means of dating sediments in the upper Magdalena Valley with and after the time of eruption of the parent andesitic and dacitic lavas in the Cordillera Central. Unfortunately, little detailed information is available as yet concerning the distribution of these lavas in Colombia, or of their place in the geological history of this region.

#### SUMMARY AND CONCLUSIONS

Small dihexahedral crystals of quartz occur as a relatively abundant detrital component in a widespread sedimentary formation in the Upper Magdalena Valley of Colombia, South America. Such an occurrence in itself is unusual, and it especially merits attention in this instance because of the abundance of well developed crystals present. The quartzoid-bearing sediment lies at the top of the Mesa formation which is thought to be latest Pliocene or earliest Pleistocene in age.

The quartzoids are considered to be of igneous origin, developed essentially under intratelluric conditions. They were liberated for accumulation in the sediment during the course of explosive volcanic eruptions and the subsequent weathering and disintegration of the parent andesitic and dacitic lavas which occur in the Cordillera Central of the Colombian Andes.

Brief observations made to date suggest that the presence of the quartzoids may offer a means of differentiating stratigraphically be-



tween the Mesa formation and the lithologically similar upper part of the Miocene Honda series; these observations require further checking.

Finally, the presence of the mineral provides a possibility of correlating the quartzoid-bearing andesitic-dacitic periods of volcanism of the Cordillera Central of the Colombian Andes with the sedimentary rocks of the Upper Magdalena Valley.

#### ICELAND SPAR IN TAOS COUNTY, NEW MEXICO

J. HARLAN JOHNSON,

*Colorado School of Mines, Golden, Colorado.*

Recently a commercial deposit of Iceland spar has been opened in New Mexico. Since such deposits are very rare and seldom last very long it seems desirable that a description of it be recorded.

*Location.* The deposit, officially known as the Iceberg Lode Mining Claim, is located in Sec. 31, T. 23 N., R. 11 E., Taos County, New Mexico, at the southern end of the old Copper Mountain Mining district, not far from the old Lithia deposits of Harding. It is about 30 miles south-southwest of Taos by road and approximately 55 miles north-northeast of Santa Fe. The operators are Messrs. E. M. Stanton and J. W. McCoy of Santa Fe, New Mexico.

*Geology.* The deposit occurs in pre-Cambrian rocks, mica schists and quartz mica schists. It occupies a tubular or conical space nearly circular in horizontal section along a fault plane. At the surface the deposit is approximately 20 feet in diameter. As of August, 1939, the workings had penetrated to a depth of from 20 to 25 feet along the southwestern side of the deposit. From the excavation it would appear that the deposit is plunging slightly to the south or southwest. The calcite appears to occupy a former cavity in the schist. It has clean-cut boundaries. The schist around the borders is altered to a clayey material. The calcite has developed as a mass of intergrown crystals of large size which completely fill the space and form a solid mass of the mineral. The surface and near surface portions of the deposit which were visible at the time of visit were discolored, more or less opaque, badly flawed, intergrown, and in some cases twinned, and were not suitable for optical use. Around the borders crystals of calcite up to  $1\frac{1}{2}$  feet across grew out into the clayey decomposed schist. To date these have supplied all of the material marketed. The outer surfaces of most of these crystals are etched and coated with clayey material. The high grade material gives a clear ringing sound when struck, quite different from the dull thud of a badly flawed piece.



*Origin.* Tertiary vulcanism was active in the general region as shown by the abundant basic lava flows which cap the mesas along the Rio Grande Valley and which filled the old valley with a thick series of flows. Local mineralization is shown by the fact that within a radius of two miles of the Iceland spar deposit there are numerous prospect holes which have yielded specimens of gold, copper, tungsten and molybdenum ores. In the opinion of the writer the deposit was formed by circulating warm waters, heated and mineralized by the cooling lavas. These travelled along the fault plane and deposited the calcite in the cavity along the fault, probably enlarging the cavity by attacking the rocks lining it. The highly altered rock and the character of the residual material around the borders of the calcite deposit support this view.

*Methods of mining.* The softness and perfect cleavage of the spar add greatly to the difficulties of mining as they practically prohibit the use of explosives or violent hammering. Technically it could be said that the deposit is worked by open pit methods with considerable "gophering" around the edges. Work is done by hand with bars, light hammers and chisels with only very small amounts of material being handled at a time.

After being extracted from the pit the calcite is carried to a work table where all colored or fractured material is immediately discarded. The balance is carefully cleaved in such a way that all imperfect material is removed from the clear flawless portions, and the latter is left in as large pieces as possible. This operation requires a high degree of skill and judgment.

Needless to say the percentage of waste to marketable material is very large and unfortunately there is practically no market for the discarded material. Some of the second-grade material, clear but slightly flawed or containing bubbles may be sold to mineral dealers for schools, museums and mineral collectors.

## BOOK REVIEW

NOMOGRAMME ZUM MINERALBESTIMMEN MIT RÖNTGENSTRAHLEN.  
TEIL I. MARTIN MEHMEL. 13 plates. Deutschen Mineralogischen Gesellschaft, Berlin, 1939, Price 5.0 R.M.

These nomograms are the first of a series planned to cover the entire field of minerals, and include the following: quartz, diaspore, hydrargillite, böhmite, halite, calcite, aragonite, dolomite, augite, hornblende, muscovite, biotite, glauconite, kaolinite, halloysite, metahalloysite, montmorillonite and feldspar. The nomograms are charts on which are plotted  $\log. \sin \alpha$  ( $\alpha$  of the Bragg equation) for the lines of the powder photographs of each mineral. Four degrees of relative intensity are indicated by the height of the lines. The charts are printed on graph paper, and are perforated so that they can be separated and used individually or mounted.

Separate charts are given for each mineral for the  $K_{\alpha}$  radiation of Cu, Cr and Fe. Since the values of  $\sin \alpha$  have the same ratios for the different wave-lengths, their plotted logarithms are exactly superposable, differing only in their location on the scale. It might be pointed out that the interplanar spacings for each line of the powder pattern are the reciprocals of  $\sin \alpha$ , and hence the logarithms of these spacings, in reverse order, are also superposable on any of the three charts, providing they are plotted on the given scale.

L. S. RAMSDELL

## PROCEEDINGS OF SOCIETIES

### MINERALOGICAL SOCIETY OF GREAT BRITAIN AND IRELAND

*Officers and Council for 1940.* President, Mr. Arthur Russell; Vice-Presidents, Prof. C. E. Tilley, Dr. W. Campbell Smith; Treasurer, Mr. F. N. Ashcroft; General Secretary, Dr. G. F. Claringbull; Foreign Secretary, Sir Thomas H. Holland; Editor of the Journal, Dr. L. J. Spencer; Ordinary members of Council, Dr. G. F. Herbert Smith, Dr. F. C. Phillips, Sir Lewis L. Fermor, Prof. H. L. Bowman, Dr. H. F. Harwood, Mr. G. E. Howling, Dr. W. F. P. McLintock, Dr. J. Phemister, Prof. H. Simpson, Mr. F. A. Bannister, Mr. S. I. Tomkeieff, Dr. S. R. Nockolds.

At the Anniversary Meeting on November 9th, Mr. Arthur Russell, President, in the Chair, the following papers were read:—

(1) *Crystallography of aramayoite*. By Dr. HARRY BERMAN and Mr. C. W. WOLFE.

Crystals of aramayoite adequate for morphological measurement were found on specimens from the type locality in Bolivia. The considerable number of forms on the crystals leads to an obvious lattice not in agreement with the previously proposed unit cell derived from  $x$ -ray measurements by Miss Yardley. The authors have, however, found an  $x$ -ray lattice yielding the smallest cell consistent with all the reflections and in agreement with the crystal form development.

The following are the crystal and  $x$ -ray constants determined:

$a = 0.8753$	$a_0 = 7.76 \text{ \AA}$	$\alpha = 100^{\circ}22'$
$b = 1.0000$	$b_0 = 8.79 \text{ \AA}$	$\beta = 90^{\circ}00'$
$c = 0.9406$	$c_0 = 8.34 \text{ \AA}$	$\gamma = 103^{\circ}54'$

(2) *Tektites and silica glass*. By Dr. L. J. SPENCER.

In a collection of 84 chemical analyses of authenticated tektites, taken from the literature, only 36 give data for specific gravity and refractive index. These are plotted on diagrams, the silica ranging from 68 to 80%. They are compared with the data for Darwin glass ( $\text{SiO}_2$  86–90%), glass ( $\text{SiO}_2$  69–98%) from meteorite craters, and the silica-glass ( $\text{SiO}_2$  98%) from the Libyan Desert.

(3) *Some australite structures and their origin*. By MR. GEORGE BAKER (communicated by Dr. F. L. STILLWELL).

Peculiar grooves and flutings on several, large, core-like australites with pronounced flaked equatorial zones are regarded as "bubble tracks" produced in flight upon molten tektite glass by hot accompanying gases.

Flaking of the equatorial zones of the australites is considered to have developed from a cutting action during flight by the frictional resistance of the atmosphere. Core-like australites formed by this process are shown to be distinct from others derived after they arrived on the earth's surface, from button and lens-shaped australites. A general definition of cores, based on their mode of origin, is advanced.

(4) *The Boxhole meteoritic iron, Central Australia*. By Dr. C. T. MADIGAN, with chemical analysis by Dr. A. R. ALDERMAN.

Fragments of iron from the Boxhole meteorite crater, which was discovered by the author in 1937, are very similar to those from the Henbury craters (about 240 miles to the SW), showing twisted surfaces, a medium octahedrite structure, and the same chemical composition (Ni 7.80%).

## NEW YORK MINERALOGICAL CLUB, INC.

*American Museum of Natural History, New York City. Meeting of October 18, 1939.*

The meeting was called to order by President Lee with 64 members and guests present. Mr. Allen Northup announced for the Excursion Committee that the Fall Excursion would take place on Election Day and the members would go to the trap quarries in Paterson, N. J.

The evening was devoted to the exhibition of specimens collected by club members during the summer and to their collecting experiences. Mr. Herbert Gray showed Nova Scotia zeolite specimens and one finely crystallized magnetite. Mr. Purfield Kent exhibited some excellent one to two inch topaz crystals on matrix from Trumbull, Conn. Mr. Merton McKown showed New Hampshire pegmatite and St. Lawrence Co., N. Y. specimens. Mr. James Morton told of his extensive collecting trip to California, with stops at Skaggs Springs for napalite and curtisite; Tick Canyon in Ventura Co., where he found howlite, priceite, ulexite and colemanite; Riverside, for phillipsite, foshagite, crestmoreite and other minerals; and, on his return, at Bisbee where he obtained tyuyamunite, shattuckite and many other minerals.

Mr. O. Ivan Lee reported the discovery of pyramidal crystals of wulfenite on a feldspar specimen from Grafton, N. H. Mr. A. N. Goddard described several of his recent trips and told of obtaining good quartz over chrysocolla from Globe, and unusually large fluorite crystals from Clay Center, Ohio, with cubes up to 14 inches on an edge.

F. H. POUGH, *Secretary*



## NEW MINERAL NAMES

### Torniellite

E. DITTLER AND F. KERNBAUER: Die Kaolinlager-stätte von Torniella (Mittelitalien). *Zeits. Prakt. Geol.*, **45**, 117-120 (1937) 4 figs.

NAME: From the locality, Torniella, Italy.

CHEMICAL PROPERTIES: A hydrous silicate of alumina. Analysis:  $\text{SiO}_2$  33.45,  $\text{TiO}_2$  tr.,  $\text{Al}_2\text{O}_3$  30.46,  $\text{Fe}_2\text{O}_3$  0.27,  $\text{MgO}$  0.02,  $\text{CaO}$  0.01,  $\text{Na}_2\text{O}$  0.03,  $\text{K}_2\text{O}$  0.04,  $\text{H}_2\text{O}$  (over conc.  $\text{H}_2\text{SO}_4$ ) 18.43,  $\text{H}_2\text{O}$  (-) 1.37,  $\text{H}_2\text{O}$  (+) 15.68,  $\text{P}_2\text{O}_5$  0.48; sum 100.24. Decomposed slowly by concentrated  $\text{HCl}$  with separation of silica.

PHYSICAL AND OPTICAL PROPERTIES: Amorphous (Debye-Scherrer diagrams show only an amorphous halo). Color, pale yellow. Soapy feel, very porous, sticks to tongue.  $\text{Hd.} = 2$ .  $G. = 2.432$ . Isotropic,  $n$  between 1.535-1.536.

OCCURRENCE: Found at Torniella, 56 km. south of Siena, as a hydrothermal alteration of a quartz trachyte dike, as a network of veins in ordinary kaolin used in ceramic and rubber manufacture.

W. F. FOSHAG

### Yttrocolumbite

Charles Lepierre: Yttrocolumbite de Mocambique. *Mem. Acad. Cien. Lisboa, Class Ciencias* **1**, 369-375 (1937).

NAME: In allusion to its composition.

CHEMICAL PROPERTIES: A columbate-tantalate of yttrium, etc.  $(\text{Fe}, \text{Mn}, \text{UO}_2)_2(\text{Cb}, \text{Ta})_2\text{O}_7 - \text{Y}_4(\text{Cb}, \text{Ta})_6\text{O}_{21}$ . Analysis: Ing. loss 1.33,  $\text{Cb}_2\text{O}_5$  31.21,  $\text{Ta}_2\text{O}_5$  21.50, Y group 14.06, Ce group 2.01,  $\text{ThO}_2$  2.65,  $\text{SiO}_2$  1.78,  $\text{TiO}_2$  1.20,  $\text{ZrO}_2$  0.25,  $\text{Al}_2\text{O}_3$  1.62,  $\text{CaO}$  1.87,  $\text{MgO}$  0.66,  $\text{Fe}_2\text{O}_3$  10.52,  $\text{MnO}$  5.08,  $\text{UO}_2$  3.10,  $\text{As}_2\text{O}_5$  0.10,  $\text{SnO}_2$  0.66,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{WO}_3$ ,  $\text{P}_2\text{O}_5$  lacking; Sum 99.60%.

PHYSICAL PROPERTIES: Color, black; luster, brilliant.  $G. = 5.49$ ,  $\text{Hd.} = 6$ .

REMARKS: Stated to be similar to ampangabite (from which it differs considerably, but is very close to yttrotantalite. *Abs.*) Also called yttro-columbo-tantalite.

W.F.F.

### Kolskite

Hydrofosterite

Karachaite

Adigeite

Deveillite

Iskildite

N. E. Efremov: Classification of the minerals of the serpentine group. *Compt. Rend. (Doklady) Acad. Sci. U.R.S.S.*, **22**, No. 7, 432-435 (1939).

NAME: From the region where it was discovered, Kola.

CHEMICAL PROPERTIES: A hydrous silicate of magnesium,  $5\text{MgO} \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ . Analysis:  $\text{SiO}_2$  43.78,  $\text{Al}_2\text{O}_3$  0.56,  $\text{Fe}_2\text{O}_3$  1.17,  $\text{FeO}$  none,  $\text{CaO}$  0.41,  $\text{MnO}$  trace,  $\text{MgO}$  37.01,  $\text{NiO}$  0.11,  $\text{CO}_2$  0.56,  $\text{H}_2\text{O}$  (+) 13.04,  $\text{H}_2\text{O}$  (-) 3.02; Sum 99.66.

PHYSICAL AND OPTICAL PROPERTIES: Color white, sometimes with pale yellow tint.  $G. = 2.401$ .  $\text{Hd.} = 2-3$ . Fibrous to compact.

Biaxial, positive,  $\beta = 1.542$ . Birefringence low. Parallel extinction.

OCCURRENCE: Found as veins in the olivinites near Saig Lake, Kola.

DISCUSSION: The serpentine group is considered to consist of a series, made up of stoichiometric combinations of two end-members, hydrofosterite  $2\text{MgO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$  and kero-lite  $\text{MgO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ . Serpentine has a theoretical formula  $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Some of these intermediate members have been named as follows:

Adigeite, Mt. Tkhach, North Caucasus,  $5\text{MgO} \cdot 3\text{SiO}_2 \cdot 2 \cdot 5 - 4\text{H}_2\text{O}$ ; Develite,  $4\text{MgO} \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ; Paradevelite,  $4\text{MgO} \cdot 3\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ; Ishkildite, Ishkildino, Urals,  $5.25\text{MgO} \cdot 4\text{SiO}_2 \cdot 3.5\text{H}_2\text{O}$ ; Kolskite, Kola Peninsula,  $5\text{MgO} \cdot 4\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ ; Karachaite,\* Shaman-Beklegen,  $\text{MgO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ .

W.F.F.

\* Abst. *Am. Mineral.*, **23**, 666-7 (1938).

### Manganphlogopite

TOYOHUMI YOSIMURA: Studies on the minerals from the manganese deposits of the Kaso Mine, Japan. *Jour. Faculty Science, Hokkaido Imperial University*, Series IV, Nos. 3-4, Geol. and Mineral., 313-453 (1939), 19 plates, 13 text figs.

A phlogopite, rich in manganese ( $\text{MnO } 18.24\%$ ) occurring in irregular foliated crystals.  $2E=0^\circ$ .  $\alpha=1.552$ .  $G.=3.21$ .

W.F.F.